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Customer No. 24113

Patterson, Thuente, Skaar & Christensen, P.A.
4800 IDS Center
80 South 8th Street
Minneapolis, Minnesota 55402-2100
Telephone: (612) 349-5740
Facsimile: (612) 349-9266

Attorney Docket No. 2950.25US02

REQUEST FOR REHEARING TRANSMITTAL

In re the application of:

	Reitz et al.	Confirmation No.: 2243
Application No.:	09/433,202	Examiner: M. A Marcheschi
Filed:	November 4, 1999	Group Art Unit: 1755
For:	PARTICLE DISPERSIONS	
Appeal Number:	2002-0227	

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Mail Stop Appeal Brief-Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Transmitted herewith are the following documents in the above-identified application, with respect to the Decision on Appeal mailed on June 23, 2004.

1. In triplicate, Request for Rehearing-13 pages and Appendix 1 (13 pages), Appendix 2 (6 pgs), Appendix 3 (1 pg); and Appendix 4 (14 pgs); and
2. Terminal Disclaimer-2 pages
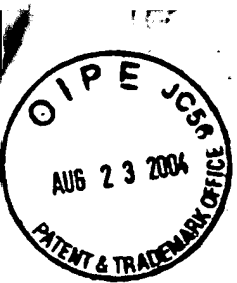
Respectfully submitted,

Peter S. Dardi, Ph.D.
Registration No. 39,650

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 16-0631.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Attorney Docket No.: 2950.25US02

Reitz et al.   Confirmation No.: 2243

Application No.:   09/433,202   Examiner: M. Marcheschi

Filed: November 4, 1999   Group Art Unit: 1755

For: PARTICLE DISPERSIONS

Appeal No.:   2004-1233

BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

REQUEST FOR REHEARING UNDER 37 C.F.R. 1.197(b)

Mail Stop Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In response to the Decision On Appeal from the Board mailed on June 23, 2004, Appellants respectfully request a rehearing of the decision under 37 C.F.R. 1.197(b). In the decision, the Board affirmed the rejection of claims 1-28 and 31. Specifically, Appellants respectfully assert that the Board made errors of law and fact with respect to affirming the rejection of claims 1-28 and 31. In view of the comments below, Appellants respectfully request reconsideration and reversal of the rejection of claims 1-28 and 31.

STATUS OF APPEAL OF PARENT APPLICATION

Appellants note that patent U.S. Patent application 09/136,483 is presently on appeal to the U.S. Court of Appeals for the Federal Circuit, appeal number 04/1074. The present

application is a continuation-in-part of application 09/136,483. This Federal Circuit appeal has been fully briefed and is pending decision by the Federal Circuit. Appellants note that some of the issues regarding the Rostoker patent are common between the parent case and the present case. Therefore, the decision by the Federal Circuit may have an impact on the present appeal.

STATUS OF THE PRESENT APPEAL

Three issues were considered in the present appeal.

1. The Board reversed the rejection of all the pending claims for obviousness-type double patenting over Reitz in view of Ishitobi and Farcas. Thus, this issue is not considered further herein.

2. The Board affirmed the rejection of all the pending claims for obviousness-type double patenting over Kambe in view of Ishitobi and Farkas. While Appellants do not agree with the Board's factual determination, Appellants have filed herewith a Terminal Disclaimer over the Kambe patent to advance prosecution of the application. In view of the Terminal Disclaimer, Appellants believe that this rejection is overcome.

3. The Board affirmed the rejection of all of the pending claims over Rostoker in view of Ishitobi and Farkas. This rejection is the subject of the present request for rehearing.

SUMMARY OF ISSUES FOR RECONSIDERATION

In summary, the Board made an error of fact with respect to interpreting the particle size distribution in the Rostoker patent. Furthermore, the Board made an error of law and an error of fact with respect to the enablement of the Rostoker patent. The separate rejection of claim 31 is considered after the more general considerations.

A.   Error Of Fact With Respect To Interpreting Disclosure In The Rostoker Patent

The Board stated its agreement with the Examiner that the Rostoker patent discloses a collection of particles having both the size and distribution within Appellants' claimed range. Decision at page 5.   Additionally, the Board presents it's own factual analysis regarding the interpretation of the Rostoker patent in an Appendix to the decision.   The Board noted that this appendix with a calculation based on the Rostoker patent was previously presented in the Appeal of the parent case, Appeal number 2001-1031.   The Board concluded from the calculation in their appendix that the Rostoker patent presented a prima facie case of unpatentability for appealed claim 1.

Since the Board has presented further evidence in their decision, Appellants also present further evidence in the form of a Declaration by an expert and further arguments in rebuttal. Based on the analysis below, Appellants maintain the Rostoker patent does not teach their claimed invention.   A Declaration by Professor Singh is presented in Appendix B to this Request for Rehearing.   When this Declaration evidence was presented in the parent case upon Request for Rehearing, the Board refused to consider the Declaration under 37 C.F.R. 1.195.   This refusal was not a justified ruling for three reasons.

First, a good and sufficient showing of why this evidence was not earlier presented is that Appellants could not refute the Board's analysis before it was made.   The Board has presented a new analysis, and it is manifestly unfair for Appellants not to be able to respond.   An Examiner does not have authority to consider evidence contrary to a Board ruling.

Furthermore, 37 C.F.R. 1.195 is contrary to the Administrative Procedures Act, 5 U.S.C. § 554.   The Administrative Procedures Act controls administrative proceedings in the Patent Office. Dickerson v. Zurko, 527 U.S. 150 (1999).   Patent prosecution generally would fall under the direction of 5 U.S.C. § 554, which relates to adjudications under the Administrative Procedures Act.   Under subsection (c)(1) of section 554, "The agency shall give all interested

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parties opportunity for - the submission and consideration of facts, arguments, offers of settlement, or proposals of adjustment when time, the nature of the proceedings, and the public interest permit." Time, the nature of the proceedings and the public interest certainly allowed the consideration of Professor Singh's Declaration under Appellants' present Request for Rehearing. Since 37 C.F.R. § 1.195 is contrary to 5 U.S.C. § 554, the Patent Office rule is unenforceable.

Third, as noted above, it would be manifestly unfair not to consider the attached Declaration. Appellants have already waited almost three and a half years from the filing of the Appeal Brief at the end of February 2001 for the Board decision on June 23, 2004. It is clearly unfair to force Appellants have to wait another four to five years for an RCE, first action, final action, appeal through decision, just to be able to refute the Board's argument, first presented in the Board's decision. The extreme unfairness of such a suggestion should be abundantly clear.

The Board noted the specification of a quality factor Q in the Rostoker patent. However, the precise meaning of this term is not clear. In support of this proposition, Appellants present a Declaration of one of the world's leading experts in this technology, Professor Singh. Professor Singh's Declaration, in Appendix A, makes it clear that the quantity "Q" is simply not well defined in the Rostoker patent. This Declaration was prepared for another application of NanoGram Corporation for a closely related Rostoker patent 5,626,715, which is identical in relevant aspects with Rostoker patent, 5,389,194 under the present rejection. (Note that the Singh Declaration inadvertently referred to the patent number as 5,128,081, which is the Siegel patent referred to in both Rostoker patents.)

With all due respect, the Board's analysis of the discussion in the Rostoker patent ignores the discussion of Q. The Board has made a reasonable attempt at giving meaning to Y. But this interpretation does not follow from the Rostoker patent. In particular, the Rostoker patent goes on to indicate the Y is related to a quality factor Q. **Q is something that is calculated from the**

actual distribution of particle sizes. Y does not have the simpler definition suggested by the Board. In particular, the Rostoker patent at column 7, lines 18-26 states that

> A quality factor "Q" is inversely related to "Y", and is a measure of the distribution of particle sizes. "Q" can be calculated as the concentration of particles at the desired size "X", divided by the range of sizes of particles at 3 db (decibles) lower than "X". Preferably, the size distribution of alpha aluminum oxide particle used for polishing exhibits a "Q" of at least 10, including 10, 50, 100, 500, 1000, 5000, or 10,000 ("Q" is dimensionless).

Due to its relationship to "Q" which is explicitly but unintelligibly defined, "Y" cannot be so easily defined as the Board has indicated. Thus, the Board's interpretation ignores the full teaching of the Rostoker patent.

Even within the Boards view, the use of +/- terminology of the Board's attempt at most interprets one parameter of the particle size distribution. Within this notation, the spread generally is a confidence interval based on a particular probability level. See Appendix 2, which are pages from a Quantitative Analysis text. The probability level is not specified. Thus, even the Board's distribution does not exclude a tail in the distribution contrary to the subject matter of Appellants' claim 1.

Appellants maintain that the distribution of particle sizes specified in the Rostoker patent cannot be interpreted in any definite way. The Board's interpretation is based on factual error due to ignoring a portion of the discussion in the Rostoker patent and imposing their own interpretation on unclear language without any basis. Accordingly, due to the inability to interpret the description in the Rostoker patent, the Rostoker patent does not prima facie render obvious claims 1-28 and 31.

B.   Errors Of Law and Fact With Respect To Enablement Of the Rostoker Patent

The Board affirmed the rejection based on a prima facie showing of obviousness. See Board decision at page 6. Assuming arguendo that the Rostoker patent does suggest Appellants' claimed invention contrary to the above section, Appellants have rebutted the enablement of the Rostoker patent to practice Appellants' claimed invention. This issue has two aspects. First, whether or not the Siegel patent, cited by the Rostoker patent, enables particles claimed by Appellants. Second, whether or not the Rostoker patent enables the formation of the claimed particles by approaches other than the methods of the Siegel patent.

1.   The Siegel Patent is Not Enabling With Respect to Appellants' Claimed Invention

First, with respect to the Siegel patent, Appellants maintain strenuously that this patent does not enable Appellants' claimed invention. The Siegel methodology is based on a cold finger condensation approach shown in their Fig. 1. This process freezes crystal domain growth faster than particle growth. Thus, for example, Figs. 5A and 6B refers to "grain size" along the right axis (5A) or the bottom axis (6B) and not particle size. Similarly, Figs. 8A - 8D refer to the materials as nanocrystalline and not nanoparticlate. The Siegel patent does not describe the particle size properties. In particular, such condensation approaches result in fused primary particles with the properties of the resulting hard fused agglomerates.

The condensation approach of the Siegel approach results in the hard fusing of the grains although the parent grains can still be recognized in micrographs. However, the dimensions of the claimed "particles" refer to free particulates. Thus, the particles of the claim refer to the hard fused agglomerates and not to the primary particles of the Siegel process. This relationship is shown schematically in Appendix 3. The hard fusing of the grains can be observed in the micrograph in the Siegel et al., article in the Journal de Physique.

As further evidence of these deficiencies of the Siegel materials, Appellants refer to U.S. Patent 6,689,190 to Pozarnsky, and assigned to Cima Nanotech, Inc. A copy of this patent is

included in Appendix 4. This inventor and company have no relationship to the present inventors and the assignee of the present invention. The Siegel patent is discussed at column 3, lines 44-65. As stated in the '190 patent, "Scrapping of particles from the deposition surface will fracture some particles and leave other agglomerated." Thus, generally the primary particles are characterized as in the Journal de Physique article, the true particle properties relate to agglomerates with widely varying properties due to the random nature of the agglomerate formation. Thus, the particle size distribution depends on the range of agglomeration that results in a very broad particle size distribution ranging from a few small, un-agglomerated particles to large agglomerates such as suggested in the lower left hand corner of the micrograph in the Siegel Journal de Physique article.

It follows that the particle properties taught in the Siegel patent fall far short of meeting the criteria of the presently claimed materials. The Rostoker patent's reference to the Siegel patent simply does not enable the formation of the presently claimed compositions of matter. The Board's suggestion to the contrary is a clear error of fact.

2. The Rostoker Patent is Not Enabling Generally

In its Decision on Appeal, the Board agreed with the Examiner that Rostoker does not state that the only method of making the aluminum oxide particles used in the claimed invention is by the method disclosed in the Siegel patent and that Rostoker merely references the Siegel patent as one known method for controllably producing the ultrafine-grained or nanocrystalline materials. Decision at page 7. First, this proposition is far from clear. Second, the Board made a clear error of law in evaluating Appellants' rebuttal evidence. At column 4, lines 25-56, the Rostoker patent refers vaguely to "recent advances" and methods recently developed with a paragraph between these references relating to the Siegel '081 patent. There is no indication whatsoever from the words in the Rostoker patent that there are other methods besides those in

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the Siegel patent. The Rostoker patent seems to be referring to the Siegel patent as the recent advances and the methods recently developed. The Patent Office's suggestions to the contrary give meaning that simply is not found in the words themselves.

Furthermore, Appellants clearly rebutted the enablement of the disclosure of the Rostoker patent with respect to the practice Appellants' claimed invention without undue experimentation using these hypothetical other unspecified approaches. The Board inappropriately shifted a larger burden to Appellants, contrary to the law, to prove patentability rather than the failure of the Rostoker disclosure to enable the practice of Appellants' claimed invention without undue experimentation. Appellants respectfully request reconsideration of the analysis of the enablement of the Rostoker patent based on the following comments.

The respective burdens in this case were discussed in Appellants' Brief. These are incorporated herein by reference. Appellants summarize the issues directly relevant for the following discussion.

The proposition is well established that the cited art only renders a composition of matter or apparatus unpatentable to the extent that the cited art enables the disputed claims, in other words, if the cited art provides a means of obtaining the claimed composition or apparatus. Assertions in a prior art reference do not support an anticipation or obviousness rejection unless the references place the claimed invention in the hands of the public. Beckman Instruments Inc. v. LKB Produkter AB, 13 USPQ2d 1301, 1304 (Fed. Cir. 1989). "In order to render a claimed apparatus or method obvious, the prior art must enable one skilled in the art to make and use the apparatus or method." Id. While a properly citable reference is prior art for all that it teaches, references along with the knowledge of a person of ordinary skill in the art must be enabling to place the invention in the hands of the public. In re Paulsen, 31 USPQ2d 1671, 1675 (Fed. Cir. 1994). See also In re Donohue, 226 USPQ 619, 621 (Fed. Cir. 1985). "But to be prior art under section 102(b), a reference must be enabling. That is, it must put the claimed invention in the hands

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of one skilled in the art." In re Sun, 31 USPQ2d 1451, 1453 (Fed. Cir. 1993)(unpublished). An **enabling disclosure** is one that allows a person of ordinary skill to practice the technology without undue experimentation based on the guidance in the disclosure along with what is well known in the art. In re Wands, 858 F. 2d 731,737, 8 USPQ2d 1400,1404 (Fed. Cir. 1988).

See also Ex parte Logan, 38 USPQ2d 1852, 1856 (BPAI 1994) (unpublished). While this Board case is not binding precedent on the present Board, it is probative of an appropriate analysis under the present facts. In Ex parte Logan, Id., the claims were rejected over a patent and a corresponding patent application. In response to the rejection, applicants argued that the cited patent and application were inoperable. In support of the applicants' assertions, a declaration was presented. The examiner dismissed the declaration as mere opinion by an interested party. The board noted that the factual evidence presented in the declaration was probative of the issues. Furthermore, the examiner did not offer any evidence or argument that the required modifications to make the previous invention functional would have been made by a person of ordinary skill in the art. The board concluded that the appellant had met their burden of rebutting the presumption of operability of the prior art patent by a preponderance of the evidence. Id. In reaching this holding the court expressly noted that, "the examiner has failed to shoulder his burden of rebutting the appellant's evidence of non-enablement/inoperability." Id.

The point is further taken in In re Payne, 606 F.2d 303, 315, 203 USPQ 245 (CCPA 1979) (citing In re Hoeksema, Supra, 399 F.2d 269, 275, 55 CCPA 1493, 1501, 158 USPQ 596, 601 (CCPA 1968)), where the Court stated, "To successfully rebut the examiner's prima facie case of enablement, it was incumbent upon Payne [appellant] to introduce affidavits or other factual evidence in support of his position. ...facts set forth in an affidavit (37 CFR 1.132) of an expert in the field suggesting that inoperativeness, would be highly probative." Id. (citations omitted).

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Under the present facts, the Examiner and the Board have mistakenly placed the burden on Appellants that there is no known way in the art to practice Appellants' claimed invention. But it is only Appellants' burden to prove that the Rostoker patent does not enable the practice of Appellants' claimed invention. Appellants have presented such evidence so that it becomes the Examiner's burden to refute Appellants' evidence. It is not Appellants' burden to prove patentability at some un-prescribed high standard just because the Patent Office misinterprets the Rostoker patent with respect to some hypothetical process to make perfect aluminum oxide particles. Under the assumptions that the Rostoker patent suggests anything about methods other than the Siegel process, it is only **Appellants' burden** to establish by a preponderance of the evidence that the disclosure in the Rostoker patent does not **enable** one of ordinary skill in the art to practice Appellants' claimed invention. Appellants have more than adequately met their burden with clear and convincing evidence, and the requirement of a higher seemingly insurmountable burden is an error of law. Assuming arguendo that the Rostoker patent even teaches Appellants' claimed invention, Appellants have presented unrefuted evidence that the Rostoker patent is nonenabling with respect to their claimed invention.

The Board's statement that the Rostoker patent does not disclose that his aluminum oxide nanoparticles can be made only by the method of the Siegel patent does not raise a prima _facie_ showing that the Rostoker patent is enabling with respect to Appellants' claimed invention. What are these other hypothetical methods? Neither the Examiner nor the Board has pointed out a single alternative method. If these are well known in the art, surely this would not be a burden on the Patent Office to point one out. While the Patent Office maintains that persons of ordinary skill in the art are well versed in these hypothetical approaches and can practice them without undue experimentation, experts in the field somehow are completely unfamiliar with these approaches. This defies logic.

The Rostoker patent only explicitly refers to the Siegel patent as a source for ultrafine powders. **While the Rostoker patent may or may not indicate that the Siegel method is the only way of making the particles, the mere suggestion that it is not limited to the Siegel method is not the equivalent of enabling disclosure.** It is the Rostoker patent that must be enabling. **The implication that there may be other unspecified ways of making the particles can only be enabling disclosure if the unspecified ways are known to a person of ordinary skill in the art and can be practiced without undue experimentation.** A person of ordinary skill in the art would need to exert at least undue experimentation unless the skilled artisan knows how to make or obtain the claimed particles without any further guidance since Rostoker does not provide any guidance.

Since the issue is whether or not a person of ordinary skill in the art would know of a way of making or obtaining the claimed particles without any guidance, Dr. Kambe's Declaration is directly on point. Dr. Kambe is certainly a person with at least ordinary skill in the art. Indeed he is an expert. He was selected by the International Center for Materials Research to lead an effort for the production of ultrafine particles based on laser pyrolysis. Dr. Kambe's experiences built on his extensive technical experiences as a senior scientist at NTT in Japan and his Ph.D. from MIT. Dr. Kambe was one of the founders of NanoGram and has served as Vice President since its founding. Dr. Kambe's Declaration directly addressed that a person of ordinary skill in the art could not practice Appellants' claimed invention based on the meager disclosure in the Rostoker patent. **Nothing more was needed to be shown.**

The Board noted that the patent is presumed valid, and the burden of proving otherwise is substantial. This general legal principle is unrefuted, but the burden is not insurmountable. First, one cannot even figure out what the Rostoker patent is saying. The Rostoker patent only describes the Siegel process for forming the particles. Appellants have rebutted the existence of other hypothetical approaches.

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Then, under the Board's own interpretation (which is completely unfounded) the Rostoker patent is laughably non-enabling. The Board in their appendix seems to say that the Rostoker patent teaches a collection of particles with all the particles between 9 and 11 nm. How can these particles possibly be made based on the teachings in the Rostoker patent? Appellants' improved approach cannot do this, at least without significant inventive redesign. Under the Board's incorrect interpretation of the Rostoker patent, the Rostoker patent is completely non-enabling.

Appellants' have clearly rebutted the enablement of the Rostoker patent with clear and convincing evidence, and thus a preponderance of the evidence supports patentability. If a person of ordinary skill in the art could practice the claimed invention without undue experimentation based on the disclosure in the Rostoker patent, the Examiner should easily be able to support that assertion with some kind of evidence. The Examiner has presented no evidence to support the enablement of the Rostoker patent with respect to Appellants' claimed invention. **Neither the Board or the Examiner have given any hints of how the Rostoker patent is enabling apart from the Siegel patent. Appellants have more than met their burden, and the rejection should be withdrawn.**

C.   Claim 31

With respect to claim 31, the Board affirmed the rejection of this claim based on the understanding that the Rostoker patent was teaching the "identical" polishing material. See Board Decision at page 10. Based on this assertion, the Board indicates that the Rostoker patent inherently teaches a polishing composition with the claimed properties. The above discussion makes it clear that the polishing compositions taught in the Rostoker patent are not substantially identical to the polishing compositions disclosed in Appellants' specification. Thus, the Board's

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inherency argument is rebutted. Since the inherency argument cannot stand, the rejection of claim 31 similarly cannot stand and should be reversed.

CONCLUSIONS

Appellants assert that the Examiner has failed to establish prima facie obviousness. To the extent that the Examiner has established prima facie obviousness, Appellants assert that they have met their burden in rebutting the Examiner's prima facie case. Appellants respectfully request the reversal of the rejection of claims 1-28 and 31 and allowance of these claims.

Respectfully submitted,

Peter S. Dardi, Ph.D.
Registration No. 39,650

Customer No. 24113
Patterson, Thuente, Skaar & Christensen, P.A.
4800 IDS Center
80 South 8th Street
Minneapolis, Minnesota 55402-2100
Telephone: (612) 349-5746

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 16-0631.

CERTIFICATE OF EXPRESS MAIL

"Express Mail" mailing label number EV 433103321 US. Date of Deposit: August 23, 2004. I hereby certify that this paper is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. § 1.10 on the date indicated above and is addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Peter S. Dardi, Ph.D.
Name of Person Making Deposit

Signature

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APPENDIX 1

Declaration of Professor Singh

Resume of Professor Singh

Applicant : Kumar et al.

Applic No.: 09/085,514

Filed : May 27, 1998

For : SILICON OXIDE PARTICLES

Docket No.: 2950.02US01

Group Art Unit: 1773

Examiner: K. Bernatz

DECLARATION UNDER 37 C.F.R. § 1.132

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

I, Rajiv K. Singh, Ph.D., hereby declare as follows:

1. I am presently a Professor of Material Science and Engineering at the University of Florida at Gainesville. Apart from my academic responsibilities, I provide consulting services through R. K. Singh Consulting Inc.

2. I received my Ph.D. degree in 1989 in Material Science and Engineering from North Carolina State University, Raleigh, NC.

3. I have been on the faculty at the University of Florida since 1990. I was promoted to Associate Professor with tenure in 1995 and to full Professor in 1997. A copy of my Curriculum Vitae is attached.

4. My recent accomplishments include receiving a National Science Foundation Young Investigator Award in 1994 and the Hardy Gold Metal for Outstanding Contributions in Material Science in

1995. I was a Distinguished Visiting Professor/Scientist at National University of Singapore (1999) and National Institute for Materials and Chemical Research, Tsukuba, Japan (2000). I am a fellow of the American Society for Materials (ASM). I am the author or co-author of more than 300 scientific articles and conference proceedings. I have co-edited seven books and guest edited five journal issues.

5. I have organized over 15 international conferences in advanced processing of materials including nano-particle science and technology and chemical- mechanical polishing (CMP).

6. I have been the Associate Director of the Engineering Research Center for Particle Science and Technology, at the University of Florida from 1994 -2001. My prime responsibility at this position was to develop advanced techniques for characterization of particles.

7. I am under a Consulting Agreement with NanoGram Corporation to provide consulting services in the area of chemical-mechanical planarization. I am not a shareholder in NanoGram Corporation. Also, I have no interest in the present patent application.

8. I have been working in the area of surface polishing and material science relating to properties of inorganic particles for many years. My laboratory at the University of Florida has performed extensive experiments in particle properties and in surface polishing. [sic]

9. I have read carefully U.S. Patent 5,128,081 to Rostoker, U.S. Patent 5,128,281 to Siegel et al., U.S. Patent 5,846,310 to Noguchi et al., U.S. Patent 4,775,520 to Unger et

al., and a passage from Ullmann's Encyclopedia of Industrial Chemistry, Vol. A23 at pp. 635-639. In addition, I have read the pending claims of the above noted patent application entitled "SILICON OXIDE PARTICLES." I did not participate in any capacity with the preparation of the SILICON OXIDE PARTICLES patent application.

10.   With respect to the Rostoker '081 patent, a theoretical type of distribution is described in the patent. This distribution as described by Rostoker has several internal inconsistencies, as described below. Additionally, this distribution described by Rostoker does not conform to any standard representation of distribution functions described in standard textbooks and standard references.

In the Rostoker distribution, X is the average particle size. Y relates to a range around X. However, Q is important since Q, in principle, defines the size distribution. Unfortunately, the discussion of Q is not internally consistent. Q is indicated in the patent to be a dimensionless quantity. Q is defined as the concentration of particles at "X" divided by a concentration of particles in a range 3dB lower than "X". The numerator of this expression has units of $\#/cm^3$, whereas the denominator term denoted by concentration of particles in a range of sizes 3dB below X has units of $\#/cm^2$. Thus, according to Rostoker's definition, Q is not dimensionless but has units of 1/cm or 1/length. For Q to be a dimensionless quantity, either both the quantities should be defined in a certain range (e.g., concentration range +1dB of X divided by concentration at range +1dB at X/2), or both the quantities should describe the concentration at specific values (e.g., at X and at 3dB below X).

Even if we assume that the patent described Q as ratios at concentrations at X and at 3dB below X (which is not the case

in the patent description), which makes Q dimensionless, there are several more inconsistencies. First, the particle size distribution is defined by only two points, which can be extrapolated into any distribution one might choose to elect. Secondly, if we define A as the point at which the concentration of particles in a range 3bd below x, then the concentration at A equals concentration at $X/10^{0.3}$. Then the concentration at A corresponds approximately to the concentration at X divided by 2. This value does not correspond to a Gaussian distribution, and the evaluation of A does not address the problems with the definition of Q. The Rostoker patent nowhere describes a 3 sigma (standard deviation) distribution. Also, the standard deviation cannot be defined for a distribution given in the patent.

It should be noted that the particle size distribution, as described in the Rostoker patent is not consistent with the particle size distributions that are frequently used in the standard particle size and technology books and publications. Examples of some of the standard book publications with which I am familiar are 1) A. Jillaventesa, S. Dapkunas and L.H. Lum, "Particle Size Characterization," NIST Recommended Practice Guide, NIST Special Publication, 960-1 (2001); 2) T. Allen, "Particle Size Measurement," 4th Edition, Chapman and Hall, London (1992); 3) B. H. Kaye and R. Trottier, Chemical Engineering, 99:84 (April 1995); 4) R. J. Hunter, "Foundations of Colloidal Science," Wiley (1998); 5) E. Kissa, "Dispersions, Characterization Testing and Measurement," and 6) B. V. Miller and R. Lines, CRC Critical Reviews in Analytical Chemistry, 20:75-116 (1988). Relevant pages from Reference 4 are attached.

The only source of powders described in the Rostoker '081 patent is the process described in the Siegel patent. However, the Siegel patent only describes the formation of nanocrystalline materials. In other words, the materials are polycrystalline materials with nanocrystalline domains. The

Siegel patent does NOT describe the formation of submicron particles. Furthermore, I am aware of no approaches for the formation of silica particles as claimed by NanoGram except for the NanoGram process, as described further below.

11.   With respect to the Unger '520 patent, this patent describes the formation of a silica gel using a two-step process. I have considerable experience with reactions that form silica gels including the Stober process and processes similar to the Unger process, from work that has been performed in my lab in Gainesville. Also, the process that leads to the formation of silica particles from alkoxide precursors is well documented in the literature, such as the texts Sol Gel Science, by C. Jeffrey Brinker and G. Scherer, Academic Press (1990) and The Chemistry of Silica, by R. K. Iler, Wiley (1979). The first step in the Unger process uses the Stober process to form a silica gel.

In the second step, increasing the particle size and removal of the porosity further refines the sol. In both the Stober and Unger processes, the hydrolysis of the alkoxide precursors occurs in basic conditions leading to formation of sol as a result of hydrolysis, polymerization and condensation reactions. The sol particle in this process typically consists of partially coalesced small clusters that form porous structures. The clusters typically are made of trimers and tetramers of silicon-hydrogen-oxygen precursors such as $SiO(OH)_3$, $SiO_2(OH)_2$, $Si_4O_6(OH)_6$, $Si_4O_8(OH)_4$, etc. After the condensation process, the clusters contain a large number of silanol groups and siloxane bonds. Several workers have made extensive studies on the use of FTIR, NMR and Raman Spectroscopy to understand the formation of the particles. Articles by Lippert et al. and Zerda et. al. are attached.

The cluster-like aggregates making the sol particles are typically smaller than 50 nm, and have a high surface area due to formation of the porous structures. Because of the high

porosity the surface area of the sols are much larger than the theoretical calculated surface area. The Unger patent also shows that the surface area of the sols of 100 - 350 m^2/gm, which is typically nearly two orders of magnitude greater the theoretically calculated surface areas based on the size of the particle measured by standard techniques such as TEM, and light diffraction measurements. Thus the sols are chemically and structurally different from a non-porous silica particle which is typically obtained from the Nanogram process. Specifically, the sols may have significant chemical variation than silicon dioxides, and the aggregates do not have the uniformity described in the NanoGram claims.

12.   With respect to the Noguchi patent, this patent describes the application of a coating onto the silica gel of the Unger patent. The Noguchi patent does not deal with the synthesis of silica particles.

13.   Pyrolytic or flame produced process is a standard method to make small particles of silica, alumina, titania, etc. There are several references that show the details on the flame-produced process. Examples include 1) Ulmann's encyclopedia; 2) Ulrich, Combustion Science Tech. 4:47-57 (1971); 3) G. W. Scherer in Better Ceramics Through Chemistry, eds. C. J. Brinker et al. (North Holland, NY 1984); 4) D. W. Schaefer, Material Research Society Bulletin, 13:22-27 (1988); 5) J.E. Martin et al., Phys. Rev. A 33:3540-3543 (1986); 6) A. J. Hurd et al., Phys. Rev. A 35:2361-2364 (1987); 7) J. D. F. Ramsay, Colloidal Surfaces 18:207-221 (1986). Copies of References 2, 5 and 6 are attached for reference. In the flame oxidation process, the small particles, which are formed by the oxidation reaction initially aggregate with each other by a ballistic process which mean that the mean free path of the aggregating species is large, compared

to the cluster size. In the second phase of the growth process, once the particles are large compared to the mean free path the trajectories of the particles change from ballistic to Brownian motion. The meandering path of the Brownian motion encourages attachment of the incoming cluster to the target periphery reacting aggregates and ramified fractal structures. Standard techniques such as visible light scattering and small angle neutron scattering have been used to show that the fractal dimension of the particles is characteristic of the diffusion limited cluster aggregation. Depending on the residence time and reactor design, the size of the primary particles may vary from 20 nm to 200 nm.

Although the primary particle size of the pyrolytic silica can be small, the particles form hard aggregates that neck in the aggregates, which make them difficult to disperse. The neck formation has been determined from transmission electron micrography (TEM). Attempts to disperse these particles result in dispersion of clusters of the fused aggregates forming individual particles. There is no way to separate the fused aggregates because the fusing results in hard bonding. Workers in field unfortunately refer to the grains that are fused together as primary particles, even though the hard fusing of these grains prevents separation of the grains as distinct particles. The actual particles are the fused entities or cluster rather than the individual 'grains. Thus, the particles are very non-uniform even if they are formed from fused grains that may be relatively uniform.

As further support for observations from my direct experience, I have attached a TEM micrograph from my lab that provide documentary evidence of these materials formed by the process described in Ullmann's Encyclopedia. The particle have an average particle size of about 20 - 50 nm and cluster sizes on average of about 250 nm. Due to the hard fusing of these

particles, the aggregates do not have high uniformity.

14.   In my experiences, I have not seen materials comparable to the materials claimed in the NanoGram patent application. Based on my extensive experience with surface polishing, I expect that the NanoGram materials will be very good materials for surface polishing since the performance is expected to depend on the uniformity of the polishing materials. Thus, the NanoGram silica particles fill a void in the types of materials available for surface polishing. While NanoGram has not commercially exploited their silica materials for surface polishing yet due to their efforts with other commercial activities, I expect that these materials will someday have a significant commercial role in improving surface polishing of substrates.

14.   I declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: Dec. 10 '01   By: _____
                                          Rajiv K. Singh, Ph.D.

A750

Summary of Accomplishments

- Research Experience, Positions held and Awards
- Management & Leadership
- Research, Education & Outreach
- Overview of Research Programs
- Research Acomplishments & Milestones
- Selected Publications

A751

RAJIV K. SINGH
Materials Science and Engineering
University of Florida, Gainesville, FL 32611
(352) 392-1032, (352) 846-0326 (fax)
Email : rsing@mse.ufl.edu

Research Interests and Experience

Innovative processing of materials; Chemical Mecahnical Planarization (CMP); Semiconductor Integration; Laser processing; Oxide thin films; Transient thermal phenomena; Superconducting and dielectric (low K and high K) thin films; Flat-Panel Displays and Phosphors; Nano Medical Devices; Diamond and related materials, Rapid thermal processing of elemental and wide band gap semiconductors; Nano particles and Particulate coatings; Modeling of transient thermal processing; Angstrom scale advanced materials characterization, Gallium nitride and diamond crystal growth, Front and back end semiconductor cleaning, Thin film batteries; Sustained Drug Release Systems; BioMEMS;

Education

Ph.D.	Materials Science and Engineering, North Carolina State University, Raleigh, 1989
M.S.	Materials Science and Engineering, North Carolina State University, Raleigh, 1987
B.S.	Chemical Engineering, Jadavpur University, Calcutta, India, 1985

Academic Positions

97-pre	Professor, Materials Sci. and Engr., University of Florida, Gainesville, Florida
95-96	Associate Professor, Materials Sci. and Engr., University of Florida, Gainesville, Florida
90-94	Assistant Professor, Materials Sci. and Engr., University of Florida, Gainesville, Florida
89-90	Research Assistant Professor, Materials Sci. and Engr., North Carolina State University, Raleigh, North Carolina

Administrative Positions

96-pre	Group Leader, Chemical Mechanical Planarization (CMP), ERC Univ. of Florida
94-01	Group Leader, Engineered Particulates, ERC, University of Florida
94-01	Associate Director, Engineering Research Center (ERC) for Particle Science & Technology

Awards/Honors

2003	*Visting Endowed Chair Professor*, University of Texas (Austin)
2001	*Fellow: ASM* (American Society of Materials)
2000	*Visiting Professor, EPFL*, Lausanne, Switzerland
2000	*Distinguished Visiting Scientist*, NIMC, Tsukuba, Japan
2000	*University of Florida Research Foundation Award*
1999	*Distinguished Visiting Professor*, National University of Singapore, Singapore
1995	*Hardy Gold Medal* from TMS/AIME for Outstanding Contributions in Materials Science
1994	*NSF Young Investigator Award*
94-97	*Visiting Fellow*, Center for Ultrafast Optical Science (CUOS), University of Michigan
1992	*Martin Marietta Innovative Research Aawrd*
1991	*IBM Faculty Development* Award
1989	*MRS Best Graduate Student* Award
1985	*Alumni Gold Medal* for Best Overall Graduating Senior from the University
1985	*Laha Silver Medal* for Best Graduate from College of Engineering

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Management and Leadership

Research leadership: Unique and diverse research background with demonstrated excellence in several areas spanning from electronic materials, ceramics, metals, polymers to pharmaceutics. Helped in establishing the $66 million ERC Center for Particle Science and Technology at the University of Florida. Developed new cross disciplinary multidisciplinary programs in the university including nano-particle science and technology, chemical mechanical polishing, diamond thin films, angstrom scale characterization, particle coatings, oxide thin films, controlled drug delivery systems. Directed multidisciplinary research groups in the area of chemical mechanical polishing (CMP) and particle coatings; developing efforts in the area nano-bio technology.

Students & Educational: Graduated 21 Ph.Ds students in the last 6 years. 6 more Ph.D students expected by end of 2003. Averaging over 3 Ph.D/ year (top 1% in College of Engineering and ten times the COE average). Managing a group of over 15 –20 graduate students and post doctoral researchers for the last 10 ten years. Graduate students have obtained jobs at leading academic institutions (University of Virginia, etc) and industrial institutions (Intel , Motorola, Samsung, etc.). Actively worked with minority student including recruitment and research training.

Infrastructure Development: Established the Characterization, Research Instrumentation and Test-Bed Facility (CRIT) facility for Particle Science and Technology, considered the best facility of its kind in the country. Also obtained NSF and matching funding ($ 3 M) to acquire new state of the art microscopes (STEM-Z and FESEM) and X-ray Diffraction capabilities, which makes MAIC (Major Analytical and Instrumentation Center), one of the premier facilities of its type in the country. Set-up state of art CMP facility, laser and lamp processing lab, plasma CVD, electrical, magnetic and optical characterization facility as a part of group research efforts.

Management Leadership: Helped develop the strategic, research and administration plan for the ERC Center. Duties include, developing budgets, and managing staff members associated with the CRIT facility. Developing research plans for multidisciplinary teams on CMP, Engineered particulates and Nanoparticle Science and Technology.

International Conferences: Organized 20 international conferences (ECS, MRS, European MRS, TMS, ASM, Engineering Foundation, IUMRS (Japan), Electrochemical Society) in the area of innovative processing of materials, including nanotechnology, chemical mechanical polishing of semiconductors, laser and ion beam processing of materials, rapid thermal processing.

Industrial Interactions: Extensive interactions and joint project development with industrial partners such as Dupont, Motorola, Dow Chemical, Lucent, Applied Materials, Motorola, 3M, Intel, IBM, Ashland Chemical, Advanced Micro Devices, Westinghouse (Northtrop Grumman), Seagate, etc.

Short Courses: Taught 8 short courses in the last 5 years in the area of thin films, CMP, particle coatings and nanoparticle technology, laser processing of materials at international conferences and at University of Florida.

Collaborations: Established a extensive and educational collaboration network leading to joint publications with more than 20 faculty members in the department, college of Engineering and the University. Developed a extensive collaborative research and educational network with the following institutions: University of Michigan, North Carolina State University, NC A&T State University, Southern University, EPFL (Lausanne), NUS (Singapore), NIMC (Japan), Keio University (Japan), Hiedelberg (Germany), Darmstadt (Germany), Oak Ridge National Labs, Sandia National Labs., Unicamp (Sao Paulo), CNRS Strasbourgh (France), IIT Kanpur (India)

Guest Editorships: Guest editor of the October MRS Bulletin 2002 Issue on Chemical Mechanical Polishing (CMP); also guest editor of 5 other journal issues in Materials Science and Engineering B, and Journal of Electronic Materials.

Technology Licensing and Spin off: Worked with the office of licensing and technology (OTL at UF) to develop and license several technologies including cleaning of semiconductors, sustained pulmonary based drug delivery systems, slurries for chemical mechanical polishing of copper/ shallow trench isolation(STI);. Spun-off two companies including Nanotherapeutics Inc (sustained drug delivery systems) and Sinmat Inc (CMP slurries).

Research, Educational and Outreach Accomplishments: Productivity and Quality

Extensive Multidisciplinary Research Background: Research activities in the last decade spanning all broad areas of materials science including electronic materials, ceramics, metals, polymers, and bio-materials. Specific areas include silicon based electronics, wide band gap semiconductors, nano-technology, sustained drug delivery, particle coatings and thin films, nano-patterning and lithography, etc.

Publications: Over 360 refereed publications including over principal author 200 journal papers; Archival publications in Science, Physical Review B, and Applied Phys. Lett. Over 50 papers in Applied Physics Letters (the highest cited journal in electronic materials). Published more than 10 journal articles in JECS/ESST in the last 5 years. Group averaging 25 journal publications/year in the last 5 years. Publication rate among top 1 % of all MSE and engineering researchers.

Research Citations: Total citations over 2500. Average number of citations/yr >200 in the last 10 years. 5 publications with over 100 citations each. Citations of research papers within the top 1% of all materials science and engineering researchers across the globe and at the University of Florida.

Books and Book Chapters: Edited 7 books in various areas of materials processing, written 11 book chapters and review articles and appointed guest editor for 5 journals issues. Presently writing 2 textbooks in the area of CMP (30% complete) and materials characterization techniques (20% complete).

Patents: Total of 15 awarded or applied with the US Patent office. Over 50 patent disclosures with the University. [Represent the highest numbers in the college of Engineering and the University and nearly 10 times the COE average]. 5 patent filed for world-wide rights.

Invited and Contributed Talks: Presented over 130 invited talks and guest lectures. Research group has presented over 350 papers in the last 10 years at international conferences.

Softwares: Written 3 user friendly softwares, including SLIM (Simulation of Laser Interactions with Materials) which is the most widely used software in the area of laser-solid interactions. Has been used by more than 50 institutions across the globe.

Research Funding: Attracted over US $2 million/yr in 00-01 and over $11 million in the last 10 years. One of the key persons for the establishment of the $66 million ERC Center for Particle Science and Technology. Also attracted substantial funding from industry (IBM, Motorola, Lockheed Martin, Sun, Ashland Chemicals, etc.). Industrial funding represents 25 % of the total award in the last 5 years.

Awards/Honors: Awarded several internationally recognized honors and awards including the Hardy Gold Medal from TMS/AIME for outstanding research contributions, ASM Fellow Award, NSF Young Investigator Award (NYI), University of Florida research foundation award. Research work featured in CNN, NY Times, Wall Street Journal and London Telegraph. Became one of the youngest full professors at the University of Florida at age 33.

Distinguished Appointments: Distinguished Visiting Professor at National University of Singapore, Distinguished Visiting scientist at NIMC (Japan), Visiting Professor at EPFL (Lausanne).

Educational Grants: Obtained educational grants (PIONEER) from NSF to train minority and graduate students. Developed IGERT proposal. Worked with minority institutions including NCA&T University and Southern University and University of Puerto-Rico.

Committee and Society Memberships: The Electrochemical Society (ECS), Materials Research Society (MRS), ASM (American Society for Materials), The Materials Society (TMS), American Vacuum Society (AVS), American Association for Advancement of Science (AAAS). Member of NSF and DOE panels, Reviewer for journals including Science, Nature, Applied Physics Letters, J. Electrochemical Society., etc

APPENDIX 2

Pages From Quantitative Analysis Text

3rd EDITION QUANTITATIVE ANALYSIS

R. A. Day, Jr.
Emory University

A. L. Underwood
Emory University

The Normal Error Curve

The limiting case approached by the frequency polygon as more and more replicate measurements are performed is the *normal* or *Gaussian* distribution curve, shown in Fig. 3.2. This curve is the locus of a mathematical function which is well-known, and it is more easily handled than the less ideal and more irregular curves that are often obtained with a smaller number of observations. Data are often treated as though they were normally distributed in order to simplify their analysis, and we may look upon the normal error curve as a model which is approximated more or less closely by real data. It is supposed that there exists a "universe" of data made up of an infinite number of individual measurements, and it is actually this "infinite population" to which the normal error function pertains. A finite number of replicate measurements is considered by statisticians to be a sample drawn in a random fashion from a hypothetical infinite population; thus the sample is at least hopefully a representative one, and fluctuations in its individual values may be considered to be normally distributed, so that the terminology and techniques associated with the normal error function may be employed in their analysis.

FIGURE 3.2 Normal distribution curve; relative frequencies of deviations from the mean for a normally-distributed infinite population; deviations $(x - \mu)$ are in units of σ.

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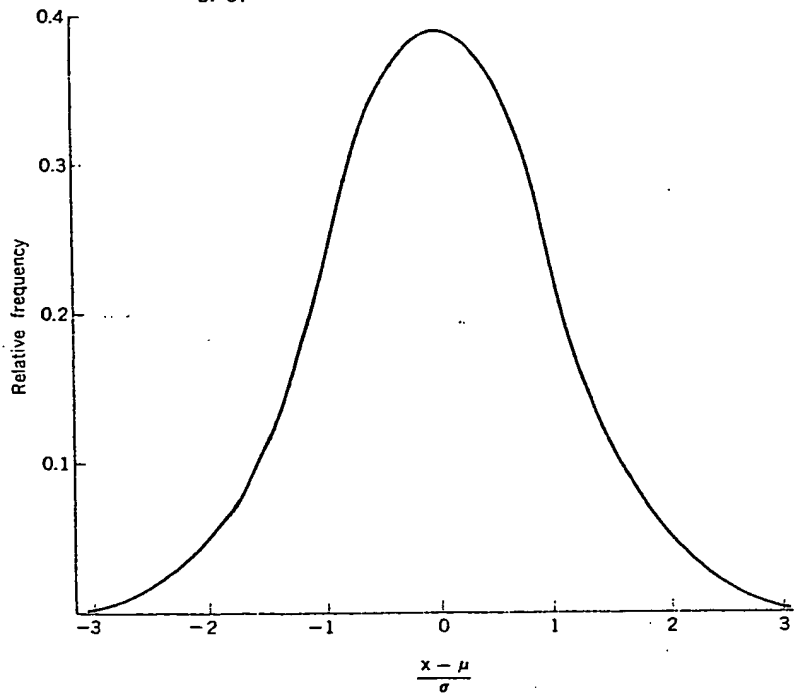
The equation of the normal error curve may be written for our purposes as follows:

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}.$$

Here y represents the relative frequency with which random sampling of the infinite population will bring to hand a particular value x. The quantities μ and σ, called the population parameters, specify the distribution. μ is the *mean* of the infinite population, and since we are not here concerned with determinate errors, we may consider that μ gives the correct magnitude of the measured quantity. It is clearly impractical to determine μ by actually averaging an infinite number of measured values, but we shall see below that a statement can be made from a finite series of measurements regarding the probability that μ lies within a certain interval. To the extent of our confidence in having eliminated determinate errors, such a statement approaches an assessment of the true value of the measured quantity. σ, which is called the *standard deviation*, is the distance from the mean to either of the two inflection points of the distribution curve, and may be thought of as a measure of the spread or scatter of the values making up the population; σ thus relates to precision. π has its usual significance and e is the base of the natural logarithm system. The term $(x - \mu)$ represents simply the extent to which an individual value x deviates from the mean.

The distribution function may be normalized by setting the area under the curve equal to unity, representing a total probability of one for the whole population. Since the curve approaches the abscissa asymptotically on either side of the mean, there is a small but finite probability of encountering enormous deviations from the mean. A person who happened to encounter one of these in performing a series of laboratory observations would be unfortunate indeed; some of us who have faith in never obtaining such a "wild" result in our own work are inclined to the view that the normal distribution as a model for real data breaks down, and that only the central region of the distribution curve is pertinent when applied to scientific measurements by competent workers. The area under the curve between any two values of $(x - \mu)$ gives the fraction of the total population having magnitudes between these two values. It may be shown that about two-thirds (actually 68.26%) of all the values in an infinite population fall within the limits $\mu \pm \sigma$, while $\mu \pm 2\sigma$ includes about 95% and $\mu \pm 3\sigma$ practically all (99.74%) of the values. Happily, then, small errors are more probable than large ones. Since the normal curve is symmetrical, high and low results are equally probable once determinate errors have been dismissed.

When a worker goes into the laboratory and measures something, we suppose that his result is one of an infinite population of such values that he might obtain in an eternity of such activity; then the chances are roughly 2 to 1 that his measured values will be no further than σ from the mean of the infinite population, and about 20 to 1 that his result will lie in the range

$\mu \pm 2\sigma$. In practice, of course, we can never find σ for an infinite population, but the standard deviation of a finite number of observations may be taken as an estimate of σ. Thus we may predict something about the likelihood of occurrence of an error of a certain magnitude in the work of a particular individual once he has performed enough measurements to permit estimation of the characteristics of his particular infinite population.

STATISTICAL TREATMENT OF FINITE SAMPLES

Although there is no doubt as to its mathematical meaning, the normal distribution of an infinite population is a fiction so far as real laboratory work is concerned. We must now turn our attention to techniques for handling scientific data as we obtain them in practice.

Measures of Central Tendency and Variability

The *central tendency* of a group of results is simply that value about which the individual results tend to "cluster." For an infinite population, it is μ, the mean of such a sample. The *mean* of a finite number of measurements, $x_1, x_2, x_3, \ldots, x_n$, is often designated $\bar{x}$ to distinguish it from μ. Of course $\bar{x}$ approaches μ as a limit when n, the number of measured values, approaches infinity. Calculation of the mean involves simply averaging the individual results:

$$\bar{x} = \frac{x_1 + x_2 + x_3 + \cdots + x_n}{n} = \frac{\sum\limits_{i=1}^{i=n} x_i}{n}$$

The mean is generally the most useful measure of central tendency. It may be shown that the mean of n results is $\sqrt{n}$ times as reliable as any one of the individual results. Thus there is a diminishing return from accumulating more and more replicate measurements: The mean of four results is twice as reliable as one result in measuring central tendency; the mean of nine results is three times as reliable; the mean of twenty-five results, five times as reliable, etc. Thus, generally speaking, it is inefficient for a careful worker who gets good precision to repeat a measurement more than a few times. Of course the need for increased reliability, and the price to be paid for it, must be decided on the basis of the importance of the results and the use to which they are to be put.

The *median* of an odd number of results is simply the middle value when the results are listed in order; for an even number of results, the median is the average of the two middle ones. In a truly symmetrical distribution, the mean and the median are identical. Generally speaking, the median is a less efficient measure of central tendency than is the mean, but in certain instances it may be useful, particularly in dealing with very small samples.

Since two parameters, μ and σ, are required to specify a frequency distribution, it is clear that two populations may have the same central tendency

APPENDIX 3

Schematic Representation of Fused Particles and Relationship with Claimed Particles

The Siegel patent describes a process that results in the fusing of the particles. The schematic sketch below illustrates the comparison of the materials from the Siegel patent and the materials claimed by Appellants.

Particles — Visible Grains Fused Within Particles
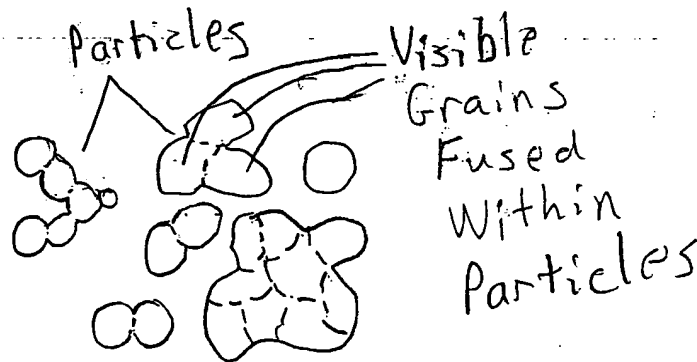
APPENDIX 4

US 6,689,190

(12) **United States Patent**
Pozarnsky

(10) Patent No.: **US 6,689,190 B2**
(45) Date of Patent: *Feb. 10, 2004

(54) **PROCESS FOR THE MANUFACTURE OF REACTED NANOPARTICLES**

(75) Inventor: **Gary A. Pozarnsky**, St. Paul, MN (US)

(73) Assignee: **Cima Nanotech, Inc.**, Woodbury, MN (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 32 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **10/026,487**

(22) Filed: **Dec. 20, 2001**

(65) **Prior Publication Data**

US 2003/0116228 A1 Jun. 26, 2003

(51) Int. Cl.[7] B22F 9/12
(52) U.S. Cl. 75/332; 75/367
(58) Field of Search 75/332, 336, 343, 75/355, 360, 367

(56) **References Cited**

U.S. PATENT DOCUMENTS

1,509,824 A	9/1924	Booth et al.	
4,576,725 A	3/1986	Miura et al.	.... 252/62.51
5,030,669 A	7/1991	Hendrickson et al.	...... 523/333
5,106,533 A	4/1992	Hendrickson et al.	...... 252/314
5,128,081 A	7/1992	Siegel et al.	.... 264/81
5,372,629 A	* 12/1994	Anderson et al.	.... 75/332
5,738,705 A	* 4/1998	Anderson et al.	.... 75/332
5,857,840 A	1/1999	Suda et al.	.... 417/302
5,958,329 A	9/1999	Brown	.... 266/176
6,267,942 B1	7/2001	Mori et al.	.... 423/338

FOREIGN PATENT DOCUMENTS

EP	0 209 403 A2	1/1987

* cited by examiner

Primary Examiner—George Wyszomierski
(74) *Attorney, Agent, or Firm*—Mark A. Litman & Assoc. P.A.

(57) **ABSTRACT**

A process and apparatus prepares and collects metal nanoparticles by forming a vapor of a metal that is solid at room temperature, the vapor of the metal being provided in an inert gaseous carrying medium. At least some of the metal is solidified within the gaseous stream. The gaseous stream and metal material is moved in a gaseous carrying environment into or through a dry mechanical pumping system. While the particles are within the dry mechanical pumping system or after the nanoparticles have moved through the dry pumping system, the vaporized metal material and nanoparticles are contacted with an inert liquid collecting medium.

15 Claims, 1 Drawing Sheet

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          ┌──────────────────┐
          │     Source       │
          │                  │
          │       of         │
          │                  │
          │  Nanoparticles   │
          └──────────────────┘
                   ↓
          ┌──────────────────┐
          │                  │
          │      Dry         │
          │                  │
          │    Pumping       │
          │                  │
          │    System        │
          └──────────────────┘
                   ↓
          ┌──────────────────┐
          │   Nanoparticle   │
          │                  │
          │   Collection     │
          │                  │
          │    System        │
          └──────────────────┘
```

Figure 1

Source
of
Nanoparticles

↓

Dry
Pumping
System

↓

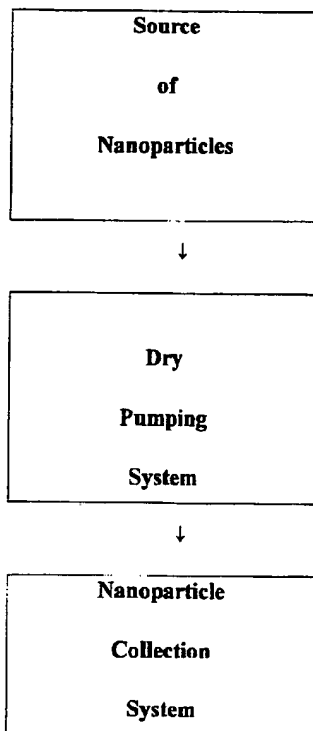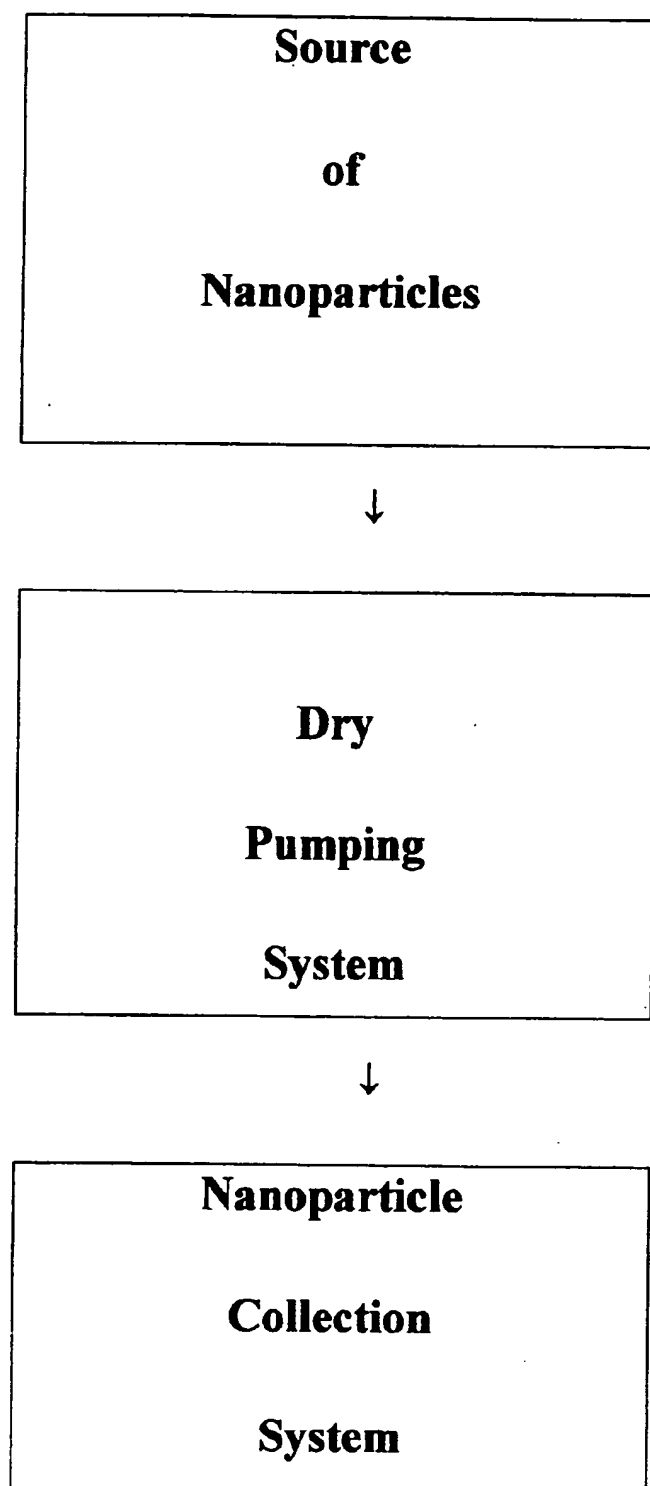| Nanoparticle |
| :---: |
| Collection |
| System |

1

PROCESS FOR THE MANUFACTURE OF REACTED NANOPARTICLES

BACKGROUND OF THE INVENTION

1. Field of the Invention

Particles, and particularly nanoparticles find a wide range of use as fillers, active media, explosives, magnetically sensitive materials, decorative materials, taggants, and reflective material. The present invention relates to the field of nanoparticle manufacture and apparatus for the manufacture of nanoparticles, and particularly for the manufacture of nanoparticles that have been reacted during manufacture, particularly surface reacted or surface coated.

2. Background of the Art

Many processes are available for the manufacture of small particles and especially small metal particles. These processes cover a wide range of technologies and exhibit a wide range of efficiencies. Some processes produce dry particles, while other processes produce particles in liquid dispersions.

Numerous references have appeared describing use of the gas evaporation technique to produce ultrafine metal powders, especially magnetic metal/metal oxide powders (often referred to as magnetic pigments). These appear to exclusively refer to a dry process and do not involve contact with liquids. Yatsuya et al., Jpn. J. Appl. Phys., 13, 749 (1974), involves evaporation of metals onto a thin film of a hydrocarbon oil (VEROS technique) and is similar to Kimura (supra). Nakatani et al., J. Magn. Magn. Mater., 65, 261 (1987), describe a process in which surface active agents stabilize a dispersion of a ferromagnetic metal (Fe, Co, or Ni) vaporized directly into a hydrocarbon oil to give a ferrofluid using a metal atom technique. The metal atom technique requires high vacuum (pressures less than 10^{-3} torr) such that discrete metal atoms impinge onto the surface of a dispersing medium before the metal atoms have a chance to contact a second species in the gas phase. In this metal atom process, nucleation and particle growth occur in the dispersing medium, not in the gas phase. Thus, particle size is dependent on the dispersing medium and is not easily controlled. Additionally, U.S. Pat. No. 4,576,725 describes a process for making magnetic fluids which involves vaporization of a ferromagnetic metal, adiabatic expansion of the metal vapor and an inert gas through a cooling nozzle to condense the metal and form small metal particles, and impingement of the particles at high velocity onto the surface of a base liquid.

Kimura and Bandow, Bull. Chem. Soc. Japan, 56, 3578 (1983) disclose the nonmechanical dispersing of fine metal particles. This method for prepares colloidal metal dispersions in nonaqueous media also uses a gas evaporation technique. General references by C. Hayashi on ultrafine metal particles and the gas evaporation technique can be found in Physics Today, December 1987, p. 44 and J. Vac. Sci. and Tech., A5, p. 1375 (1987).

EPA 209403 (Toyatoma) describes a process for preparing dry ultrafine particles of organic compounds using a gas evaporation method. The ultrafine particles, having increased hydrophilicity, are taught to be dispersible in aqueous media. Particle sizes obtained are from 500 Angstroms to 4 micrometers. These particles are dispersed by ultrasound to provide mechanical energy that breaks up aggregates, a practice that in itself is known in the art. The resulting dispersions have improved stability towards flocculation.

Other references for dispersing materials that are delivered to a dispersing medium by means of a gas stream

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include U.S. Pat. No. 1,509,824, which describes introduction of a molecularly dispersed material, generated either by vaporization or atomization, from a pressurized gas stream into a liquid medium such that condensation of the dispersed material occurs in the liquid. Therefore, particle growth occurs in the dispersing medium, not in the gas phase, as described above. Furthermore, the examples given are all materials in their elemental form and all of which have appreciable vapor pressures at room temperature.

U.S. Pat. No. 5,030,669 describes a method consisting essentially of the steps: (a) vaporizing a nonelemental pigment or precursor to a nonelemental pigment in the presence of a nonreactive gas stream to provide ultrafine nonelemental pigment particles or precursor to nonelemental pigment particles; (b) when precursor particles to a nonelemental pigment are present, providing a second gas capable of reacting with the ultrafine precursor particles to a nonelemental pigment and reacting the second gas with the ultrafine precursor particles to a nonelemental pigment to provide ultrafine nonelemental pigment particles; (c) transporting the ultrafine nonelemental pigment particles in said gas stream to a dispersing medium, to provide a dispersion of nonelemental pigment particles in the medium, the particles having an average diameter size of less than 0.1 micrometer; wherein the method takes place in a reactor under subatmospheric pressure in the range of 0.001 to 300 torr.

U.S. Pat. No. 5,106,533 provides a nonaqueous dispersion comprising pigment particles having an average size (diameter) of less than 0.1 micrometer dispersed in an organic medium That invention provides an aqueous dispersion comprising certain classes of inorganic pigment particles having an average size (diameter) of less than 0.1 micrometer dispersed in a water or water-containing medium. The dispersions require less time for preparation, are more stable, have a more uniform size distribution, a smaller number average particle diameter, fewer surface asperities, and avoid contamination of dispersed material due to the presence of milling media and the wear of mechanical parts, these problems having been noted above for dispersions prepared by conventional methods employing mechanical grinding of particulates. Additionally, no chemical pretreatment of the pigment is required in order to achieve the fine particle sizes obtained in the final dispersion. The pigments of the dispersions are found to have narrower size distributions (standard deviations generally being in the range of ±0.5 x, where x is the mean number average particle diameter), are more resistant to flocculation (i.e., the dispersions are stable, that is they are substantially free of settled particles, that is, no more than 10% of the particles settle out for at least 12 hours at 25° C.), and demonstrate superior overall stability and color as demonstrated by lack of turbidity, by increased transparency, and by greater tinctorial strength, compared to mechanically dispersed pigment dispersions. Furthermore, the method requires no mechanical energy, such as ultrasound, to break up aggregates. Aggregates do not form since there is no isolation of dry ultrafine pigment particles prior to contacting the dispersing medium. The dispersions of any organic or inorganic pigment or dispersion that can be generated from a pigment precursor, are prepared by a gas evaporation technique which generates ultrafine pigment particles. Bulk pigment is heated under reduced pressure until vaporization occurs. The pigment vaporizes in the presence of a gas stream wherein the gas preferably is inert (nonreactive), although any gas that does not react with the pigment may be used. The ultrafine pigment particles are transported to a

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liquid dispersing medium by the gas stream and deposited therein by bubbling the gas stream into or impinging the gas stream onto the dispersing medium.

U.S. Pat. No. 6,267,942 describes a process for manufacture of spherical silica particles. Silica gel particles to be dispersed in a mixed solution of an alkali silicate and an acid are required to have an average particle size of from 0.05 to 3.0 micrometers. In a case where the average particle size of the silica gel particles is smaller than 0.05 micrometers, mechanical strength of the spherical silica particles to be obtained will be low, and irregular particles are likely to form, such being unsuitable. Similarly, in a case where the average particle size of the silica gel particles is larger than 3.0 micrometers, mechanical strength of the spherical silica particles to be obtained will be low, and irregular particles are likely to form, such being unsuitable. The more preferred range of the average particle size of the silica gel particles is from 0.1 to 1.0 micrometers. A more recent advance in particle coating technology is the use of fluidized bed systems, and in particular, magnetic fluidized bed systems such as that shows in U.S. Pat. No. 5,962,082 (Hendrickson et al.). There, a magnetic field fluidizes a bed of magnetically responsive particles. The magnetically responsive particles and/or other particles carried into a fluidized bed are coated with a material (e.g., a liquid) provided in the fluidized environment. The coating composition may even be transferred from the magnetic particles to non-magnetic particles. This process provides excellent control over the coating thickness, can produce large volumes of coated particles, and provides many other advantages.

U.S. Pat. No. 5,958,329 describes a method and apparatus for producing nanoparticles (there defined as from 1 to 50 nano-meter diameter particles) at a high rate. Two chambers are separated by a narrow duct. A source material is provided from a lower chamber where the source material is heated (e.g., to vaporization and then continuously fed into an upper chamber. In the upper chamber, nanoparticles are nucleated, the nanoparticles being formed when the vapor fed from the lower chamber collides with a gas (inert or reactive) in the upper chamber. A cooled deposit site (e.g., defined as finger 107) collects the particles, which are then scraped from the collection site. The particles are said to move to the collection site in a natural connective flow stream.

U.S. Pat. No. 5,128,081 describes a method of preferential phase separation of aluminum oxide nanocrystalline ceramic material. The nanoparticles are collected on a cold surface (20). Following oxidation of the particles, a vacuum chamber (in which the particles were formed) is evacuated and the oxide particles are collected and consolidated under various atmospheric conditions, such as vacuum and selectively with oxygen and/or air.

The collection process in these particle manufacturing and particle treating processes is cumbersome, inefficient, costly, time-consuming and damaging to the particles. For the collection process, the chamber must be opened and particles scraped from the deposition surface. This requires a long term shut down of the system. Scraping of particles from the deposition surface will fracture some particles and leave others agglomerated. Scraping can also damage the deposition surface. The small elongate finger deposition surface allows for the production and collection of only small amounts of materials layering of collected particles reduces the efficiency of deposition onto the surface. Coating of the particles can be done, but only as re-dispersion of the dried and agglomerated particles.

An alternative method of particle collection is filtration. This is performed by placing in sequence a source of

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particles, a filtration medium and a vacuum source. The filter has two surfaces, one front surface facing the particle source and the other rear surface facing the vacuum source. The reduced pressure at the rear surface allows the higher pressure at the font surface to push gas and particles against the filter where the particles are entrapped. There are a number of problems in a filtration system, particularly when it is used with nanoparticles. For example, to collect nanoparticles having an average particles diameter of from 1 to 100 nanometers, the largest pore size in the filter must be less than about 1 nanometer. It is difficult to maintain an effective pressure across that filtration surface, even before particles start collecting. As nanoparticles collect on the filter surface, gas flow (and pressure driven movement) become more restricted, fewer particles can collect, and process efficiency diminishes. The particles clog pores rapidly and particles do not collect efficiently.

U.S. Pat. No. 5,857,840 describes a vacuum pump system for making a closed container vacuous, comprising a vacuum pump and a dust collector provided on a pipe connecting the closed container and the vacuum pump, the pipe including:

a main pipe having a first main pipe which connects the closed container and the collector and a second main pipe which connects the centrifugal collector and the vacuum pump;

a bifurcated pipe which is branched out from the first main pipe and connected to the vacuum pump;

a metal mesh dust collector disposed on the bifurcated pipe; and

pipe switching means for switching over between the main pipe and a bifurcated pipe.

The dust collector is provided intermediate the source of dust and vacuum pump, which may include a dry pump.

SUMMARY OF THE INVENTION

A particle collection system with increased collection efficiency for the collection of nanoparticles comprises a source of particles, a dry pumping system, and a particle collection surface. The position of a dry pumping system in advance of the particle collection surface maintains a particle moving effort, without wetting particles and causing them to agglomerate, and increases collection efficiency. The source of particles usually comprises an evaporation/condensation process with an inert gas flow into the evaporation/condensation system. Particles are then reacted by introducing a reactive gas with or in addition to the inert gas within or after at least partial condensation of particles. By providing the reactant as a vapor that can intimately associate or react with the surface, excellent control over the degree and uniformity of reactions, including in situ polymerization on the surface of particles, is greatly enhanced.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 shows a system for the manufacture of reacted nanoparticles according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

A particle collection system with increased collection efficiency for the collection of nanoparticles comprises a source of particles, a dry pumping system, and a particle collection surface. The position of a dry pumping system in advance of the particle collection surface maintains a particle moving effort, without wetting particles and causing

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them to agglomerate, and increases collection efficiency. The source of particles usually comprises an evaporation/condensation process with an inert gas flow into the evaporation/condensation system. Particles are then reacted by introducing a reactive gas with or in addition to the inert gas within or after at least partial condensation of particles. By providing the reactant as a vapor that can intimately associate or react with the surface, excellent control over the degree and uniformity of reactions, including in situ polymerization on the surface of particles, is greatly enhanced.

The placement of the collection units between the nanoparticle source and vacuum pumps causes severe problems in maintaining system vacuum and related high evaporation rates. Wet collection systems are difficult to operate in a vacuum environment; however, the operation of wet collection systems provides slurries in a number of different solvents, which can be post-treated by in-situ polymerization techniques to coat the nanoparticles. The resulting slurries can be post treated by in-situ polymerization methods to coat the particles in solution. The particles in the resulting slurries can be coated with fluoropolymers, such as teflon and polyvinylidene difluoride (PVdF). This differs from earlier work using of high pressure reactor technology to provide a teflon or PVdF coating. This is the first known application of these polymers in an in-situ polymer coating process.

A source of nanoparticles is provided. The source may be a primary source where particles are being manufactured (e.g., sputtering, spray drying, aerial condensation, aerial polymerization, and the like) or may be preferably provided by evaporation and condensation within a process stream. The source of nanoparticles may also be a secondary source of particles, where the particles have been previously manufactured and are being separately treated (e.g., coating, surface oxidation, surface etching, and the like). These nanoparticles are provided in a gaseous medium that is of a sufficient gas density to be able to support the particles in flow. That is, there must be sufficient gas that when the gas is moved, the particles will be carried. With nanoparticles (e.g., particles having number average diameters of 0.5 or 1 to 100 nm, preferably 1 to 80 nm, or 1 to 70 nm, and as low as 1 to 50 nm) only a small gas pressure is needed, such as at least 0.25 Torr although higher pressures greater than 0.25 Torr, greater than 0.4 Torr, greater than 0.6 Torr, and greater than 0.75 Torr greater than 0.9 Torr are preferred.

The gas-carrying medium may be or have been reactive with the particles or may have some residual reactive materials in the gas. It is preferred mainly for preservation of carrying and collecting surfaces, that the gas is relatively inert to the apparatus environment. Gases such as nitrogen, carbon dioxide, air and the like are preferred.

The propulsion system for the gas carrying medium and the nanoparticles is a dry mechanical pumping system for gases. A dry pumping system is used to prevent contamination of the particles by lubricants. These dry pumping systems for gases are well known in the semiconductor industry for conveying air, particulate and vapors without collection occurring in the pump. They are pumping systems that utilize oil-less seals to maintain vacuum conditions at the pump inlet. Examples of such dry pumps and dry vacuum pumps in the literature are found in U.S. Pat. No. 4,452,572 (Robert Evrard) generates a dry vacuum when acting as an additional stage to a conventional vacuum pump. It cites a tubular diaphragm that admits a pressure differential across the diaphragm to allow the diaphragm to conform to the contour of the pumping chamber body and thus expel gas via a top valve. U.S. Pat. No. 5,971,711

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describes a control system for pumps, including dry pumps based on a Roots system pump.

U.S. Pat. No. 6,050,787 provides a dry pump comprising a magnetically responsive elastic tube stretched onto, thereby sealing to, a shaft with inlet and outlet ports at or adjacent to it's ends of the tube. Local to the inlet port a magnetic field is generated in the enclosing body. This field is substantially concentric to the tube, which then responds by expanding circumferentially towards the magnetic field. This creates a volume between the tube and shaft, the length of tube outside the influence of the magnetic field remains sealed upon the shaft. Subsequent movement of the magnetic field along the axis of the pump gives transport of this volume and any media now enclosed within it from the inlet port to the outlet port, whereupon reduction of the magnetic field results in exhaustion of the volume. This cycle results in pumping action.

Other general disclosures of mechanical dry pumps are provided in U.S. Pat. Nos. 6,090,222; 6,161,575; 5,846,062 (which describes a screw type dry vacuum pump having dual shafts is disclosed, whereby the process gas is transported through three compartments, a gas admittance pump section, a central drive motor section, and a gas discharge pump section. By placing the drive motor in the center of the pump, it becomes possible to design a pump having the dual shafts supported only at one end, thus enabling to mount the rotors at the free ends of the pump which are closed with end plates which can be removed easily for servicing the pump sections. Synchronous operation of the dual shaft pump by magnetic coupling enables to lower power consumption and to extend the range of operable pressures.

The collecting medium for the nanoparticles may comprise electrostatic surface collectors, electrostatic filter collectors, porous surfaces (e.g., fused particle surfaces), centrifugal collectors, wet scrubbers, liquid media collectors and physical filter collectors. The liquid media collectors) with subsequent separation of the liquid and the particulates) are more amenable in the practice of the present invention. Also know as wet scrubbers, these liquid collection media are more amenable to this arrangement due to process and safety factors allowing more volatile solvents to be utilized away from the formation chamber for the nanoparticles. Wet scrubbers also provide slurries suitable for post-treatment and polymer coating by in-situ polymerization, particularly in the case of fluoropolymer coatings. Examples of this are Teflon, Polyvinylidene difluoride (PVdF), and their respective copolymers. This differs from earlier work in the field using high pressure reactor technology to achieve the polymer coating. This technique can be used to coat metallic particles, pigments, oxides, and nitrides. This is the first know application of these polymers in the in-situ polymer coating process.

The use of the present arrangement of nanoparticle source, dry pump and collector has been found to increase particle collection efficiency by as much as 100% in comparison to the conventional source, filter pump system, even where the same nanoparticle source is present, the same filter and the same pump is used in the different order. The utilization of this arrangement of the pumping scheme may also benefit the collection of the nanoparticles. By injecting low volatility solvents into the inlet of the pump with the nanoparticle loaded gas stream, the dry pump may also be utilized as a wet scrubber with better than 90% collection efficiency. Suitable solvents are the various available Isopar® media and Purasolv® media.

Small particles of metals are prepared by an evaporative method with a unique collection and reaction method that

increases the production efficiency of the process by dramatic degrees. The process comprises evaporating a metal and then providing a mechanical pump that either draws the gas phase metal into a liquid condensation-collection zone or combines a liquid condensation-collection zone within the mechanical pump. The non-metal gaseous material remaining after condensation removal of the metal material is withdrawn from the material stream, while the liquid condensing phase with the condensed metal particles is separated, the liquid condensing phase carrier removed, and the particles collected. As compared to known prior art methods, the use of the intermediate positioned mechanical pump or contemporaneous mechanical pump and condensation-collection zone increases the overall collection/manufacturing efficiency of the process by at least 25%.

The existence of nanoparticulate materials such as metals, organic materials, metal oxides, halogenides and other pigments has been known for several years now; however, the production of these materials is still extremely low from the existing processes. This has had a detrimental effect on the availability and therefore the utilization of these materials in various products, especially in the area of energetic materials concerning nanoparticulate aluminum. Several of the military and civilian applications of this material have remained unattained due to the lack of suitable large scale supplies of this material to incorporate into the end products or at least proof out these materials in research and development work.

The most frequently used technique to form nanophase materials, such as metals, is the inert gas condensation, or dynamic gas condensation, method (Siegel, R. W. and Eastman, J. A., Material Research Symposium Proceedings, 132, p. 3, 1989; and Granquist, C. G. and Buhrman, J., J. Appl. Phys., 47, p. 2200, 1976). In this technique, a metal is vaporized and recondensed by contact with a low pressure flux of inert gas. The typical method used to melt and vaporize the metal to be converted into nanophase metals has been resistive heating. Through the use of either a tungsten or tantalum heating element or an intermetallic ceramic bar, metal, such as aluminum, is evaporated from conductive heating by contacting the hot surfaces of the material. The use of intermetallic ceramics is favored over the metallic heating elements due to the ability of metals may corrode other metals by an alloying process. This causes shorting of the resistive circuit by overamping, etc. This has resulted in the use of the intermetallic materials (AlN, BN and TiB₂) in aluminum evaporation.

"Flash" evaporation is that condition where the molten metal is superheated beyond the boiling point of the aluminum at certain conditions and is instantly converted to vapor (Learn, A. J., Thin Solid Films, 20, p. 261, 1974). In a high vacuum system, it is relatively easy upport both the melting and vaporization of the metal if the appropriate amounts of energy are available. For the resistive heating method; however, there is only enough energy available to vaporize small amounts of material at one time. This is often why wire feed mechanisms are commonly used with resistive heating/vaporization methods (Rynec, D. M., Solid State Tech., 11, p. 48, 1968; Learn, A. J., J. Electrochem. Soc., 123(6), p. 894, 1976). As a conductive method of heating and vaporization, the energy transferred by conduction in the resistive heating methods is maximized by use of a small contact area that continually evaporates small amounts of material supplied by the wire feed mechanism. The wire feed mechanism is uniquely suited to the requirements of the resistive heating/vaporization techniques, and the

evaporation/production rates are then determined by the speed of the wire feed mechanism matching, but not exceeding the amount of metal that could be evaporated by the conduction-driven methods. Even at high voltages and feed rates; however, the end production rate is not an industrially suitable method for the manufacture of aluminum nanoparticles. A typical resistive bar operates at 4 volts and 830 amps and dissipates a power of 3324 watts. The temperature generated is ~1500° C. A typical evaporation rate is 0.10 grams/min per bar. This is quite low and batteries of resistive bars are often used to form an aggregate production rate suitable for vapor coating. This is sufficient for vapor coating substrates to a depth of less than two-tenths of a micron as is typically done for Mylar polyester and nylon web coatings in commerce. Although this would suffice for a vapor coating operation, it is not a scaleable procedure for large scale nanoparticle production.

Resistive heating also has other drawbacks as well. It has been observed that a temperature gradient appeared in the resistively heated bar from convection when exposed to the inert gas needed to nucleate the vapor into the nanoparticles. The ends of the bar would be hotter than the center where the metal would be fed onto the bar. This has two outcomes. First, the excess energy needed to vaporize the aluminum metal is lost due to convective heating of the gas stream. Second, the temperature of the bar also drops considerably due to the convective losses. This drop in temperature puts the overall operating parameters of the system (temperature, pressure) into undesirable areas. In relative comparative terms, undesirable effects correspond to the slow evaporation of water below its boiling point versus the rapid evaporation and steam evolution that occurs when the water is superheated beyond its boiling point where the water is converted directly into steam.

The additional pressure that occurs from the introduction of a gas stream into the system is also a factor. Most rough vacuum pumps can reach ultimate pressures of less than 50 mTorr in a closed vacuum system without the introduction of gas into the system. The addition of gas flow to the vacuum chamber changes this base pressure considerably as the expansion of the ambient condition gas at near vacuum yields a higher gas volume that must be pumped from the system. This base pressure will also increase with the presence of line expansions and constrictions that occur with the presence of vacuum chambers and traps in the system (Brunner, W. F. and Batzer, T. H., "Practical Vacuum Techniques", Krieger Publishing Co., New York, 1974; and O'Hanlon, J. F., "A User's Guide to Vacuum Technology", Wiley, N.Y., 1980. This increase in base pressure coupled with the temperature drops observed with gas contact on the resistively heated bar puts the operating parameters of the system below the vapor pressure curve.

For this inert gas condensation process to work at a reasonable production rate, a method of vaporizing the metal in this case, aluminum, must be found that allows a high operating temperature for the system while maintaining the proper gas flow and pressure characteristics in the system.

A high vaporization rate of material may also be effected by inductive heating. With the ability to couple directly into the metal itself to heat and vaporize it, it is an obvious technique to utilize in a large scale production method. Due to the ability to input the energy available directly into the metal itself, there may also be a larger operating window in terms of temperature and pressure. A small scale induction unit used may be a Mark 6, 10 kHz, 15 kW Pillar unit. Due to coil and line losses, only 80% of the 15 kW is available (12 kW) for introduction into the metal charge in the

induction crucible. With the antiferroelectric behavior of aluminum metal, only 30 to 50% of this power can couple effectively with the metal charge to heat and vaporize it. The coupling of this technology with the melting and vaporization of metals has been well established since World War II (Davies, E. J., and Simpson, P., "Induction Heating Handbook", McGraw-Hill, London, 1979; Davies, E. J., "Conduction and Induction Heating", Peregrinus, London, 1990). The results from the 15 kW unit employed here can be scaled to a standard 600 kW unit or higher power depending on the custom design and manufacture available for these systems. Vacuum chambers and induction coils are readily available or can be manufactured easily. This comprises the first part of the non-public system developed during this project. The second part of the system is the vacuum pumping system, which has been well established and developed from the vapor coating and semiconductor industries. The third part of the system is the collection of the metal nanoparticles and their dispersion into liquid media. The last part of the system is the fluoropolymer coating portion of the process where the nanoparticles are coated with the protective polymer coating to prevent oxidation.

Collection of the nanoparticles is also a problem for the production of nanoparticulate slurries. Most previous attempts for the production of nanophase materials consisted of vaporizing the metal feedstocks at ultralow vacuum conditions and collecting the nanoparticles formed on a liquid nitrogen cold finger system by thermophoresis or the walls of a large volume expansion chamber by impingement and settling (Siegel, R. W. and Eastman, J. A., Material Research Symposium Proceedings, 132, p. 3, 1989; Granquist, C. G. and Buhrman, J., J. Appl. Phys., 47, p. 2200, 1976). This has several disadvantages in collection including the inability to form unique unagglomerated nanoparticles. Although mean particle sizes of <10 nm are claimed, this is mainly the primary particle size of the crystallites of the material which are formed. These crystallites are agglomerated to particle sizes which are much higher than this mean crystallite size during the collection process. This collection method also leads to oxidation problems with pure metal systems as the surfaces of the dry, reactive nanoparticles need to be passivated in some manner before further handling. This is typically done by oxidizing the outer surface of the nanoparticles by the controlled admission of oxygen to the chamber to form a thin oxide layer to eliminate the possibility of their burning in uncontrolled atmospheres. This oxidation essentially destroys useful fuel in the bulk of the nanoparticle. Most passivation layers for aluminum metals are up to 10 nm in depth. For a 30 nm or lower diameter particle, this is most of the metal present. However, thinner layers of the passivation oxide have been achieved with difficulty (Granquist, C. G. and Buhrman, J., J. Appl. Phys., 47, p. 2200, 1976; Aumann, C. E., Skofronick, G. L. and Martin, J. A., J. Vac. Sci. Tech. B, 13(3), p. 1178, 1995. Dixon, J. P., Martin, J. A., and Thompson, D., U.S. Pat. No. 5,717,159, (February 1997).

Collection in liquids yields two advantages. First, it protects the surface of the particles from contamination or oxidation by providing a temporary liquid cover over them. Second, the process provides a slurry that can be handled in a safe fashion. The liquid dispersion medium can be a solvent, polymer monomer, or prepolymers (Dixon, J. P., Martin, J. A., and Thompson, D., U.S. Pat. No. 5,717,159, (February 1997); Hendrickson, W. A., Wright, R. E., Allen, R. C., Baker, J. A., and Lamanna, W. M., U.S. Pat. No. 5,030,669.

Previous work with evaporated pigments has found that the immediate dispersion of pigment nanoparticles is often beneficial in the formation of a stable dispersion of nanoparticles in the collection liquid. The collection systems previously utilized were sparge units that bubbled the dust-laden gas through the collection liquid and scrubbed the nanoparticle materials from the gas itself.

Fluoropolymer coatings to prevent contamination of the various nanoparticles were initially employed in the background work on the present project. The application of these coatings was done by an in-situ growth of the coatings on the aluminum nanoparticles in the non-aqueous slurries formed. This is similar to the work where polystyrene, polyaniline and other coatings were applied to inorganic oxides, sulfides or chalcogenides. The use of a fluoropolymer was to provide a pliable, noncracking coating to the outside of the reactive nanoparticle surface. In contrast to the former particle coating experiments, these polymerization reactions need to be run in high pressure reactors to liquefy the gaseous fluoromonomers and allow the polymerizations to proceed at a reasonable rate. However, this technology is well developed, and standard equipment and parts are available for this process. Fluoropolymers, such as polyvinylidene fluoride (PVdF) and its copolymer Viton®, have been produced commercially on an industrial scale since the early 1960's (Rexford, D. R., U.S. Pat. No. 3,051,677; and Lo, E. S., U.S. Pat. No. 3,178,399.

Although a suitable system for the production of small scale samples, the prior art collection process was not considered a viable method for the large scale production of this material.

A substantially improved vacuum system was designed that deepened the system vacuum to values appropriate to flash evaporate metals utilizing the induction unit power. This did increase the production rate of the system. Although the evaporation rate and corresponding nanopowder production rate were increased substantially, the ability to collect the nanoparticle materials by sparging the dust-laden gas through a collection liquid was limited severely. To achieve the higher production rate through deepening the system vacuum, a higher gas flow also occurred, which increased the amount of gas sparged through the collection liquid by a factor of four. With the lower flow rate (~1 liter/min) at the lower production rates, the collection of the nanopowder was nearly 80–90% using the sparge collection vessels. With the higher flow rate of gas through the sparge vessels, the collection of the nanopowder dropped severely and the entrainment of the slurry in the gas stream also became a problem as the liquid was blown out of the collection system.

The slurry outflow out of the collection vessels was never halted, even after upsizing the sparge vessel to approximately 5 gallons. This size of vessel was too large to handle easily or safely with the nano-metallic slurry present. Mesh packings in the collection vessels were also employed to stop the entrainment of the slurry from the collection vessel, but also failed to halt the entrainment of the liquid in the gas stream. A two gallon collection vessel with a cyclone attached to recycle the gas entrained slurry back to the vessel was eventually employed to sparge the gas and re-collect the liquid slurry, but the collection efficiency of the sparging collection unit dropped to only 20% of the total powder evolved. Combined with losses to the system from powder build-up, this was unacceptable.

A derivation of a proprietary technique was utilized to overcome this collection problem. Former work arrived at

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the use of high power aspirators to both collect the nano-particles produced in liquids and also to supply vacuum to the evaporation chamber at the same time. Although it worked sufficiently well at the lab scale, it was difficult to implement at the pilot plant scale for materials other than pigments. This technique is now significantly improved in this application with some variations to increase the system vacuum. With the use of the combined liquid collection/vacuum supply system, many of the prior obstacles to high rate evaporation and liquid collection were overcome. This current capability of the system is a collection efficiency of nearly 90% of the material contacting the scrubbing system.

The evaporation rate of 10 gm/min for aluminum smetal indicates that there is considerable energy loss in the system and that only 25–33% of the total power of the system is being used to vaporize the material. These losses may be occurring in heating the crucible, heating the cold aluminum to its melting and boiling points or in general convective heat losses to the gas stream in the system.

Although the evaporation rate of material per hour may be in the 500–600 gm/hr range, other factors impact on the efficiency and productivity of the system. The crucible for this work holds ~20 gms of material. Although a minor amount of time is lost in preheating the aluminum metal, the aluminum metal has been nearly vaporized after approximately two minutes. The overall production rate; however, is also impacted by the time needed to replenish the crucible after each successive charge is gone. The initial wire feed spools utilized in the system were aluminum 1100 grade ³⁄₆₄ inch diameter wire with a weight of 0.6 grams/foot of wire. This required that nearly 40 ft of wire be fed into the crucible for each metal charge. This would require more than 30 minutes with the normal mechanical wire feeds utilized in aluminum vaporization operations, but the simple hand driven mechanism on the present system allowed the feed time to the crucible to be reduced to one-third of that time.

The large-scale production of material from this system also has consequences in terms of particle size control and materials corrosion. There are often references in the literature about the ability to tailor the particle size of nanoparticles formed by the inert gas condensation method by increasing the back pressure of inert flux gas in the system (Siegel, R. W. and Eastman, J. A., Material Research Symposium Proceedings, 132, p. 3, 1989; Granquist, C. G. and Buhrman, J., J. Appl. Phys., 47, p. 2200, 1976; Aumann, C. E., Skofronick, G. L. and Martin, J. A., J. Vac. Sci. Tech. B, 13(3), p. 1178, 1995).

The coating and reactive aspects of the invention may be used with any material that can be evaporated below 3000° C. and condensed to a solid at room temperature, including metals, organics, ceramics, glasses, inorganics generally and the like, although the primary description herein will be directed towards metals. The first requirement for any prospective metals to be utilized in the system is that of melting point. For a system that can only reach maximum temperatures of 1600–1700° C., refractory metals, such as tantalum, molybdenum, and tungsten, are beyond the system's capability. High melting point metals, such as titanium, zirconium and platinum, are also beyond the systems energy capability. The inductive field of the system would mainly heat these metals to temperatures of ~1600° C. as was observed on crucible tests for some of these materials.

With ferromagnetic metals, such as iron, cobalt and nickel, utilization of the present technique is possible, but difficult to perform at the same rates as aluminum due to their high melting points. Although there is an area where

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iron can be flash evaporated from the system, the extremely low pressure needed would preclude the utilization of all but very high capacity vacuum systems. Although other types of pumps, such as diffusion pumps, could be used to achieve the low vacuum pressures needed in conjunction with roughing pumps, these types of pumps do not operate under the gas flow conditions needed to nucleate the nanoparticles from the gas phase. Although this would be the preferred equipment in a static vacuum system, the addition of gas flow eliminates their usage. The evaporation of these ferro-magnetic metals would be difficult without high capacity systems and even their dispersion would be problematic. These nanoparticles were formed at a very low production rate in the older production systems (e.g., 1–2 grams/day).

A full-scale system would have four major pieces of equipment to produce either a solvent or solvent/prepolymer nanoparticle slurry. The four main pieces of equipment would be 1) the induction power source, 2) the vacuum chamber and feed systems, 3) the vacuum pumps and 4) the liquid collection system. This is for the largest induction unit presently made on a commercial basis

Compared to other more costly equipment that vendors have claimed can do the same tasks, this system has an exceedingly low cost for capital equipment in this project. Increases of production or efficiencies of the system during scale-up could have massive impacts on price of the product materials.

In addition to the detonation or military applications, this fully developed system for the production of nanoparticles, particularly pigment or metal nanoparticles particles and especially aluminum nanoparticles and their dispersions will find significant outlets in forming pigment dispersions for paints, toners, inks, colorant systems, plastic/resin coloration, coating colorization, pharmaceutical coloration, and the like.

Dry, coated and uncoated nanoparticulate pigment samples (5 grams) have also been manufactured for commercial primer and toner usage. Dry uncoated samples of pigment nanoparticle inkjet inks for the production of printing inks and toners, and other nanoparticulate pigment dispersions have been evaluated for use in inkjet inks.

The production and efficiency of collection rate of nano-particulate materials has been increased significantly to rates that are scaleable to large sized production lots by practice of the invention. The utilization of nanophase metal particles in particular technical areas may also be dependent, in part, on the dispersion of the nanoparticles into particular liquid media of choice. An added bonus of the program has been the improved ability to collect and disperse the nanoparticles into different liquid media. This liquid media can be solvents, carriers, reactive compositions, coating solutions, oils, polymer monomers or prepolymers or mixtures of these liquids. This feature, in addition to the increased collection/condensation efficiency is an added advantage of the inventive process over other processes presently available in this field. The dispersion of these nanoparticles into these different liquids aids in their ease of processing and also in the protection of any reactive surfaces from oxidation and even physical damage.

The technology that has been developed by the inventors also has applications outside the narrow confines of any specific metal or alloy, but is generically useful for any metal or alloy that can be provided in a vapor state and which can be condensed by cooling in a liquid medium. The particles can also be collected wet in different liquid media in which they can form stable dispersions for use in a wide variety of technical areas such as discussed above.

In this application:

"ultrafine" means having a mean number average diameter of less than 0.1 micrometer, preferably in the range of 0.001 to 0.1 micrometer, more preferably in the range of 0.001 to 0.08 micrometer, most preferably in the range of 0.001 to 0.05 micrometer; and having a standard deviation in the range of ±0.05 x, where x is the mean number average particle diameter;

"gas evaporation technique" means any method involving the evaporation of a metal, metals or alloys in the presence of a non-reactive gas to provide ultrafine metal or alloy particulate.

The present invention is capable of providing an aqueous or nonaqueous metal or alloy dispersion comprising metal or alloy particles or an aqueous dispersion of these particles, the particles having a means number average particle diameter in the range of 0.001 to 0.1 micrometer (1 to 100 nanometers), preferably dispersed in a dispersing medium. Preferably the mean number average particle diameter is in the range 0.001 to 0.08 micrometer (1 to 80 nanometers) and most preferably 0.001 to 0.05 micrometer (1 to 50 nanometers). The dispersions can contain pigment from 0.001 to 50% by weight, preferably from 0.001 to 25% by weight, and more preferably, from 0.001 to 10% by weight of the total composition. Narrow size distribution ranges of less than ±25% or ±15% of the average diameter are also able to be formed and are desirable.

A non-limiting example of the manner in which a dispersion according to the present invention may be prepared includes:

a) vaporizing a metal, metals or alloy in the presence of a non-reactive gas stream (or introducing the vaporized metal into a non-reactive gas stream) or a reactive gas stream to provide ultrafine particles (especially metal and alloy particles),

b) transporting the ultrafine particles suspended in the gas stream by a mechanical pump to a liquid dispersing medium, as for example, a mechanical pump located before the dispersing medium or containing the liquid dispersing medium, the gas containing the particles being forced into the liquid dispersing medium or the gas containing the particles intimately contacting the dispersing medium, to provide a dispersion of particles in the medium (with vaporized metal condensing in the liquid medium),

c) the gas (absent the particles) is then separated from the dispersing medium (e.g., by bleeding out the gas, allowing the gas to rise to an exit area within a chamber, etc.), and

d) the dispersing medium is then used to carry the collected metal or alloy particles as a dispersion or the dispersing medium is then optionally being separated from the pigment particles to provide non-dispersed metal or alloy particles.

Metals having a vaporization temperature below 3000° C. are well known in the art, and include, for example, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Y, La, Ac, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Al, In, Tl, Sn, Pb, mixtures and alloys of these metals and even the lanthanides and actinides, if desired.

Several methods are available for characterizing a particle dispersion. The most common involves the particle size distribution expressed as the weight percentage of particle falling within a given size range. Typical size limits for metal particles desired in the practice of this invention are about 0.01 to 1.00 micrometer (10 to 1000 nm).

These values are indicative of the overall range of particle sizes typically encountered after conventional dispersion techniques. The distribution of particle sizes is dependent on the means of particle formation. Where mechanical milling is used to comminute the particles, extremely wide distributions result.

In the present invention, the vapor phase of evaporated particles and the particles themselves may be generated by any evaporative process such as subliming pigments or any other evaporation process for pigments at subatmospheric atmospheric or supcratmospheric pressures in the presence of a non-reactive gas to generate ultrafine metal or alloy particles and then effecting direct introduction into a dispersing medium such as described herein, has not been taught. Where the term "metal" is used herein, it is intended to include metals, mixtures of metals and alloys.

As noted above, dry organic pigments have also been generated by H. Toyotama (supra) using a gas evaporation technique. The reference teaches the need to provide mechanical energy in the form of ultrasound, which shows that, once isolated, the dry pigment particles have an affinity for each other and, therefore, energy must be provided to break the aggregates apart. One additional aspect of the present invention that can be used to differentiate the generation of metals from the pigment process of H. Toyotama in that the vacuum provided is dynamic and a constant flow of non-reactive gas stream is swept past the metal vaporization source, at rates that can be generally in the range of 25 to 2000 SCCM (standard cc's per minute) for a laboratory scale apparatus, during metal evaporation. Thus, while Toyotama is dependent on the residence time of the ultrafine particles in the growth zone (see Granqvist and Buhrman, J. Appl. Phys., 47, (1976), p. 2200) to determine the ultimate particle size obtained for a given pressure, the instant invention provides a secondary means for particle migration from the growth zone, i.e., convective currents are important as in H. Toyotama (supra) but also the non-reactive gas stream assists in carrying particles from the growth zone. Thus, at a given pressure, the present invention provides metal particles that are significantly smaller than pigment particles achieved in a static (Toyotama) system. Furthermore, the metal particles of the invention are introduced into the dispersing medium before they have a chance to aggregate, thus removing the need for external mechanical energy, such as ultrasound, to achieve a dispersed state.

Dispersing media useful in the present invention include any liquid, aqueous (where the metal does not rapidly react with water at collection conditions) or nonaqueous (for most metals). Fluids having a viscosity up to 100,000 P or more are envisioned as useful. Preferred viscosities are less than 5000 cP, more preferably less than 3000 cP, and most preferably less than 1000 cP. Representative dispersing media include water, gelatin/water emulsion, alcohol/water, including mixtures such as ethanol/water, glycerol/water, etc. and polar organic liquids such as acetone, 2-butanone, cyclohexanone, 2-undecanone, methanol, ethanol, isopropanol, glycerol, ethylene glycol, ethyl acetate, alkanes (e.g., hexane, cyclohexane), methyl methacrylate, 2-hydroxyethbyhnethacrylate, chloroform, methylene chloride, alkylalkanolamines, such as 2-dimethylaminoethanol, 1-dimethylamino-2-propanol, 1-diethylamino-2-propanol, 2-dimethylamino-2-methyl-1-propanol, and 2-dibutylaminoethanol, and combinations thereof.

Useful nonpolar organic liquids include hexane, a mixture of isoparaffinic hydrocarbons, b.p. 156° C.–176° C. (Isopar G®, Exxon, Houston, Tex.), benzene, toluene, xylenes,

styrene, alkylbenzenes, and combinations thereof. In addition, liquid polymers such as polydimethylsiloxane (e.g., DC200™ MW$_n$=200, Dow Chemical, Midland, Mich.), polydimethyl-co-methylphenylsiloxane (e.g., DC 704™, Dow Chemical), polyethylene glycol (e.g. Carbowax® 200, Carbowax® 400, and Carbowax® 600, MW$_n$=200, 400, and 600, respectively, Union Carbide Corp., Danbury, Conn.), a polymer comprising perfluoropolyether segments (LTM™, 3M, St. Paul, Minn.), and polycaprolactones (Placcel™ 305, 303, 308, MW$_n$=300–850, Daicel Chemical Ind. Co. Ltd., Tokyo, Japan) may be used.

Additionally, external heat may be applied to melt a solid (e.g., a polymer, a wax, or any low melting organic compound such as naphthalene) and generate a liquid dispersing medium suitable for use in the present invention. Examples of solids that may be used include paraffin wax, low molecular weight polyester (e.g., FA™-300, Eastman Chemical Co., Rochester, N.Y.), and polyethylene.

The dispersing medium may be a pure liquid or a mixture of liquids and may contain additional ingredients, including inorganic and organic soluble materials and mixtures thereof. Such additives include surface-active agents, soluble polymers, insoluble particulates, acids, bases, and salts.

By surface active agent is meant an additive that has a preferred spatial orientation at an interface, e.g. large molecules having a hydrophilic head group and a hydrophobic tail (e.g. OLOA™ 1200, Chevron Corp., Richfield, Calif., and Amoco™ 9250, Amoco Chemical Co., Naperville, Ill.). The weight percent of surface active agent to dispersing medium can be from 0 to 20%, preferably 0 to 10%, and more preferably 0 to 5%. Other surface active agents useful in the present invention are well known to those skilled in the art.

Soluble polymers useful as additives in the present invention, for example, in the manufacture of pigmented films, include polystyrene, polystyrene-co-butadiene, poly (methyl methacrylate), poly(ethyl methacrylate), poly(butyl acrylate), poly(4-vinylpyridine), poly(2-vinylpyridine), poly (vinylpyrrolidone), poly(2-hydroxyethyl methacrylate), poly (ethylene terephthalate), polystyrene-co-4-vinylpyridine, polystyrene-co-2-vinylpyridine, polyethyleneglycol, poly (ethylene oxide), poly(propylene oxide), polyethylene, polypropylene, poly(acrylonitrile), poly(phenyl vinylene carbonate), poly(vinyl acetate), poly(vinyl alcohol), poly (vinyl trifluoroacetate), poly(vinyl chloride), poly(ethylene-co-propylene adipate), poly(1,4-phenylene sebacate), poly (3,5-dimethyl-1,4-phenylene sulfonate), poly (.beta.-alanine), poly(hexamethylenesebacamide), poly(vinyl cymantrene-co-4-vinylpyridine), etc. The percent of soluble polymer in the dispersing medium may be from 0 to 70% by weight, preferably 0 to 50%, more preferably 0 to 30%, and most preferably 0 to 25%, or each range with at least 0.5% minimum therein. Other polymers useful in the present invention are known to those skilled in the art.

Insoluble particulates useful as additives in the dispersing medium of the present invention, for example, in the manufacture of pigmented composite structures, include latex particles, kaolin, alumina, glass microspheres, and other common fillers known to those skilled in the art. The weight percent of filler compared to the total dispersion can be from 0 to 80%, preferably 0 to 60%, and more preferably 0 to 50%. The high specific heat additives may assist in moderating the temperature of the dispersing medium.

The non-reactive gas can be virtually any gas that does not react with the metal or other material forming the nanoparticle under the conditions of the experiment. Typical choices

are He, Ne, Ar, Xe, and N_2. Mixtures of two or more non-reactive gases can also be used. When modification of the metal particles is desired as is desired here, a reactive gas can be introduced through a gas inlet that is positioned so as to minimize reaction with the bulk material in the crucible and allow thorough mixing of the reactive gas with the particles entrained in the gas stream, thereby allowing reaction with the particles to occur. The reactive and non-reactive gases generally are at room temperature, but the temperature can be elevated or reduced as desired. The term reactive includes 1) direct reaction with the particles, as in the case of metals, for example, with O_2, NO, NO_2, CO_2, CO, AsH_3, H_2S, H_2Se, NH_3, trimethylchlorosilane, methylamine, ethylene oxide, water, HF, HCl, or SO_2, or combinations thereof, to form the corresponding oxides or other compounds; 2) wetting, as described in UK Patent 736,590 to increase dispersibility in which particles are exposed to the vapor of a volatile liquid which may be identical to the dispersing medium or may be miscible with the dispersing medium, prior to contacting the bulk dispersing medium so as to create a solid/liquid interface while the particles are suspended in the gas stream; and 3) adsorption, in which a volatile substance is introduced in the gas prior to contacting the dispersing medium, similar to wetting, but the substance is either not a liquid under normal conditions (atmospheric pressure and 25° C.), the substance is not miscible with the dispersing medium, or else the substance acts to protect the surface of the ultrafine metal particles from the dispersing medium or additives within the dispersing medium. Typical substances that could be adsorbed include polymers such as poly(methylmethacrylate) and polystyrene, and surface active agents.

Temperatures for evaporation of metals useful in the method of the present invention depend on the type of pigment being used and generally range from 25° C. to around 500° C. when organic pigments are used and from 25° C. to around 1200° C. or even 25° C. to 3000° C.

Temperatures of the dispersing medium useful in the method of the present invention depend on the particular medium being used and generally range from −78° C. to 400° C., preferably from −50° C. to 300° C., and most preferably from 0° C. to 200° C.

Pressures useful in the method of the present invention range from about 0.001 to 300 torr, preferably 0.01 to 200 torr, more preferably from 0.01 to 100 torr, and most preferably from 0.1 to 50 torr. The composition of the combination non-reactive and reactive gas stream can be from about 5 to 100% non-reactive gas or combination of non-reactive gases, preferably from 25 to 100%, more preferably from 50 to 100%. A reactive gas introduced through an additional inlet downstream from the evaporation source can be present as a component in the gas stream in a percent ranging from 0 to about 95%, preferably from 0 to 75%, and more preferably, 0 to 50%.

An apparatus for providing dispersions of ultrafine metal particles comprises:

    a) a furnace connected to a collection vessel, the furnace containing a heating means (e.g., resistive, inductive, e-beam, infrared, laser, plasma jet) and adapted to contain at least a first and optionally a second gas inlet tube, said second tube being located downstream from said first tube, and a mechanical pump for evacuating the furnace and directing the gas phase carrying evaporated metal particle to the collection zone or vessel the zone and/or vessel containing a dispersing medium;

    b) an optional system (e.g., a ceramic, plastic, or metal crucible or slab that can be preloaded with material or

which can be continuously or batch-wise fed during operation of the apparatus, or the electrodes can be the means) for introducing a metal into the furnace and evacuation thereof;

c) optionally a system (e.g., a micro metering valve, electronic flow controller, or gas dispersing tube) for introducing through the first inlet tube a first, non-reactive gas stream into the furnace;

e) an evaporating or gas phase producing system (e.g., energy input as by e-beam, infrared, laser, inductive, resistive, or plasma jet) for evaporating of generating a gas phase of the metal particles into the first gas stream;

f) a collection/condensation medium between or coincident with the evaporating or gas phase producing system for allowing condensation of the vaporated metal particles (e.g., decreasing the temperature, raising the pressure, changing the chemical nature of the non-reactive gas, controlling the length of the transfer tube, controlling the gas flow rate, or combinations thereof) in the first gas stream to produce a dispersion of ultrafine metal particles in the first gas stream in a dispersing medium in the collection/condensation zone;

g) optionally, a system (e.g., tube, valve, pipe, a micro metering valve, electronic flow controller, or gas dispersing tube) for introducing into the furnace or after the furnace but before collection through the second inlet tube a second, reactive gas stream, to allow reaction with the metal particles, to provide ultrafine reacted metal particles;

h) a region within the system for collecting particles in the collection/condensation vessel (e.g., bubbling into or impinging particles onto the dispersing medium).

Reactive materials include compounds, compositions and materials that chemically react directly with the metal or which coat the metal particles and then may themselves be reacted, by themselves or with other materials or by specific activation. Examples of such reactive materials are materials in vapor form such as acids, oxidizing agents, reducing agents if the metal has been undesirably oxidized), polymerizable materials (e.g., monomers in vapor form), ambifunctional materials that can react with one end of a molecule to the metal and have another end of the molecule available for reaction with another material or surface.

The innovation described herein involves at least a repositioning of the vacuum pump in the system which a) allows a higher level of vacuum to be achieved, b) reduces the particle size of the metal particles formed and c) increase the efficiency of wet collection of the nanoparticles formed to as much as greater than 95%. This is a substantial improvement over the prior art where the wet collection of pigment particles occurred prior to the source of vacuum in the system. In prior art, the efficiency of the wet collection was a maximum of 50% at low gas flow rates (e.g., 2 liters/minute). This modest level of efficiency drops substantially at higher gas flow rates through the system. The present invention can use higher flow rates, higher than 3 liters/minute, higher than five liters/minute, higher than seven liters per minute, higher than 10 or 20 liters/minute and even higher than 50 liters per minute and provide collection efficiency rates of greater than 80%, greater than 90% in some cases, and still as high as 95% in some other cases.

With the presence of nanoparticles in the gas stream, oil sealed mechanical pumps do not function in this altered processing scheme. Dry, mechanical pumps that utilize gas-purged bearings are the most preferred for this application.

tion. These pumps can tolerate the presence of large amounts of particulate in the gas streams that are being pumped and convey the particulate from the inlet to the exhaust of the pump. Various models can also convey various liquids and vapors through their interiors. These pumps are in widespread usage in the semiconductor industry. For this application, scroll pumps did not provide sufficient performance without powder buildup in the interior of the pump. Dry lobe and screw pumps provided a sufficient amount of vacuum for the evaporation processes without powder buildup. Most preferred were dry screw pumps that could tolerate the presence of low volatility liquids (Isopar®, Dowanal®, Purasolv®, etc.) in the pump mechanism. These liquids could be injected into the inlet of the vacuum pump and used as scrubbing/condensation/collection media for the nanoparticles formed. The collection efficiency of this method is >95% of the nanoparticulate material entering the vacuum pump. Higher volatility liquids and viscous liquids as the collection/dispersion/scrubbing media (e.g., prepolymers, polymers, monomers) required the use of an alternate wet collection system, such as a venturi scrubber, positioned after the vacuum pump. These pumps typically operated at 1–10 Torr utilizing gas flows of up to 50 liters/min of an inert gas at 100° C.

The innovation described involved a repositioning of the vacuum pump in the system to a) allow a higher level of vacuum to be achieved, b) reduce the particle size of the metallic nanoparticles formed and c) increase the efficiency of wet collection of the nanoparticles formed to as much as greater than 95%. This is a substantial improvement over the prior art where the wet collection occurred prior to the source of vacuum in the system. In prior art, the efficiency of the wet collection was a maximum of 50% at low gas flow rates. This efficiency drops substantially at higher gas flow rates through the system.

With the presence of nanoparticles in the gas stream, oil sealed mechanical pumps do not function in this altered processing scheme. Dry, mechanical pumps which utilize gas-purged bearings are the most preferred for this application. These pumps can tolerate the presence of large amounts of particulate in the gas streams that are being pumped and convey the particulate from the inlet to the exhaust of the pump. Various models can also convey various liquids and vapors through their interiors. These pumps are in widespread usage in the semiconductor industry. For this application, scroll pumps did not provide sufficient performance without powder buildup in the interior of the pump. Dry lobe and screw pumps provided a sufficient amount of vacuum for the evaporation processes without powder buildup. Most preferred were dry screw pumps that could tolerate the presence of low volatility liquids (Isopar®, Dowanal®, Purasolv®, kerosene, diesel fuel, etc.) in the pump mechanism. These liquids could be injected into the inlet of the vacuum pump and used as scrubbing media for the nanoparticles formed. The collection efficiency of this method is as much as >95% of the nanoparticulate material entering the mechanical vacuum pump. Higher volatility liquids and viscous liquids (prepolymers, polymers, monomers) required the use of an alternate wet collection system, such as a venturi scrubber, positioned after the vacuum pump. These pumps typically operated at 1–10 Torr utilizing gas flows of up to 50 liters/min of an inert gas at 100° C.

A wire feed mechanism replenished the crucible after each metal charge had been evaporated and converted to nanoparticles by inert gas condensation. The dust-laden gas was then conveyed to and through the dry screw vacuum pump, where it was either scrubbed out by injection of low

volatility solvents at the inlet of the pump (i.e., within a pump chamber and therefore coincident with entrance to the pump) or passed through the pump (and therefore after entering and passing through the pump) and scrubbed out by a wet collection unit behind it. The slurry formed could then be used in the intended final product or used for further treatment of the nanoparticles formed.

EXAMPLE 1

Aluminum Nanoparticle Collection in Isopar® G

The system as described above was used to evaporate aluminum wire and form nanoparticles from it. In this example, aluminum was used, but pigments (both organic and inorganic) have also been used, with merely adjustments in the evaporation temperature and the selection of the dispersant medium. Isopar® G was used as a collection fluid for the system and injected at rates of 0.25–0.5 liter/min into the inlet of the vacuum pump. Argon gas flow was maintained at a level of 20 l/min to yield a background pressure of ~8 Torr in the chamber. The nanoparticles formed were collected at 95% efficiency in the liquid slurry at a primary particle size of 0.03 microns. Reactive gas is introduced at any point prior to collection to enable reaction of the surface of the particle.

EXAMPLE 2

Copper Nanoparticle Collection in Purasolv® BL

The system as described above was used to form copper nanoparticles utilizing copper wire. In this example, copper was used, but pigments (both organic and inorganic) have also been used, with merely adjustments in the evaporation temperature and the selection of the dispersant medium. Purasolv® BL was used as the collection media at an injection rate of 0.25–0.5 l/min into the vacuum pump. Argon gas flow was maintained at a level of 10 Torr within the evaporation chamber. The nanoparticles formed were collected at >95% efficiency in the dry screw pump at a primary particle size of 0.01 microns. Reactive gas is introduced at any point prior to collection to enable reaction of the surface of the particle.

EXAMPLE 3

Collection of Aluminum Nanoparticles in HTPB/ Heptane Solution

The system as described in FIG. 1 was used to evaporate aluminum wire, form aluminum nanoparticles and collect it into an Hydroxy Terminated Polybutadiene (HTPB)/heptane mixture. In this example, aluminum was used, but pigments (both organic and inorganic) have also been used, with merely adjustments in the evaporation temperature and the selection of the dispersant medium. The aluminum nanoparticles formed were conveyed through the dry screw pump and collected in a venturi scrubber operating behind the pump. The nanoparticles were collected into the resin/ solvent slurry at an efficiency >90%. The primary particle size of the aluminum nanoparticles formed was 0.03 micron. The % of the HTPB in the heptane slurry was 10 wt %. With a ratio of 3 to 1 weight resin to aluminum nanoparticles, the mean agglomerate size in the resin was ~0.25 microns. The heptane could then be evaporated off of the resin to yield a useable nanoparticle-loaded HTPB slurry. Reactive gas is introduced at any point prior to collection to enable reaction of the surface of the particle.

As shown in FIG. 1, apparatus 10 for providing the present invention dispersions comprise furnace 12 having therein crucible 14 supported by electrodes 15 connected to an external power supply, not shown, and containing vaporizable material 16. Gas inlet tube 18 allows non-reactive gas 19 to be introduced into furnace 12 to envelop and assist in formation of fine particles 20 and facilitate their transportation through transfer tube 22 by way of the intermediate primary dry mechanical pump 23 to collection vessel 24. Collection vessel 24 contains liquid dispersing medium 26 into which transfer tube 22 having tube end 21 allows transported pigment particles 20 and non-reactive gas 19 to bubble into medium 26 (FIG. 1) or it allows transported pigment particles 20 and non-reactive gas 19 being transported through transfer tube 22 having tube end 21 to impinge upon medium 26. Transfer tube end 21 can be used in FIG. 1 apparatus. Condensor 32 is provided to return any evaporated liquid from liquid medium 26 back to collection vessel 24. Condensor 32 is connected to trap 38 and pump 40. Pump 40 is used to evacuate the entire apparatus 10 prior to and during use. Bypass valve 34 and bypass tube 36 allow for facile evacuation of furnace 12 prior to onset of pigment 16 evaporation. Valves 42 and 44 allow isolation of apparatus 10 from pump 40.

Other reactor designs to provide dispersions of the invention can be envisioned, including a rotary metal atom reactor such as described in Metal Vapour Synthesis in Organometallic Chemistry, J. R. Blackborow and D. Young, Springer-Verlag (N.Y.), 1979 and a spinning disk assembly such as described in Jpn. J. Appl. Phys., 13, 749 (1974), as long as the location of the mechanical pump is after the system for generating the gas phase of metal particles carried in the gas phase and between or coincident with the condensation/ collection zone. Both types of reactors could be used to generate dispersions of metal particless. Additionally, metal that can be evaporated directly to generate discrete metal molecules may be used in these reactors to prepare dispersions of the present invention.

In addition to resistive heating, other means of applying heat to the pigment or pigment precursor may be envisioned. These include laser heating, inductive heating, plasma jet, plasma arc discharge, laser flashing, sputtering, and others known to those skilled in the art.

In a preferred embodiment the present invention provides metal nanoparticles, dispersions of metal nanoparticles, which metal nanoparticles are solid (i.e., solidified) dispersions of metal particles in a polymer, the particles having a mean average particle size of less than 0.1 micrometer (100 nanometers). In addition, the particles have a narrow size distribution and the dispersions are transparent, and are resistant to flocculation. The amount of pigment present in a coating is generally in the range of 0.001 to 50.0 weight percent, 0.001 to 30.0 wt percent, 0.001 to 10.0 wt percent, 0.001 to 5.0 wt percent, 0.001 to 3.0 wt percent, 0.001 to 1.0 wt percent, and more preferably 0.001 to 0.1 wt percent. Generally no surfactants or other dispersing aids are required when using the ultrafine particles of the present invention.

There are distinct advantages for using ultrafine particles as colorants in manufacturing processes and products. For medical devices or layers that provide critical physical or chemical properties, it is prudent to minimize the amount of metal particle required to achieve a specified level of a particular secondary property to preserve those properties; hence, a well dispersed nanoparticle of metal is desirable. Dispersions of ultrafine metal particles are more stable than their larger sized counterparts. This resistance to agglom-

eration prior to solidification of the liquid polymer makes the manufacturing of a articles less sensitive to uncontrollable environmental factors. Smaller particles form more stable dispersions/suspensions than do larger particles.

The dispersions of the present invention can be used to prepare articles by means of any type of article forming, such as casting, coating, toning, printing, molding, including injection molding and extrusion processes, casting, including spin casting, etc. Such articles include fibers and molded articles including conductive layers, structural elements, explosive materials, composites, electromagnetic responsive or resistive materials and the like. Coated dispersions of the present invention can be used to prepare high quality metallic graphic arts constructions such as sublimation type thermal transfer recording media, and any other applications where dispersed material is useful. The coating can be accomplished by any means known in the art including bar coating, knife coating, thermal mass transfer, curtain coating, meniscus coating, slot coating, etc. A wide variety of particle coating processes are known in the art. For larger size particles, e.g., for 1 mm or greater, the simplest, most cost effective process is direct immersion of particles in a coating composition (e.g., liquid, gel, powder, etc.) and removing the coated particles from the coating environment (with drying or agitation, as needed to fix the coating and separate the particles). Particles may be carried on a conveyor belt and sprayed or otherwise coated with coating compositions. Particles may be projected of dumped into a deposition coating environment (e.g., spray chamber, vacuum deposition chamber, electrostatic chamber, etc.) where the coating is applied. Mixtures of particles and coating compositions may be mixed, then sprayed to fix of dry the coating on the surface of particles.

As previously noted, many different types of reactive materials may be combined with the nanoparticles of the invention, and that combining of materials may be effected at various stages of the process. The selection of the time of addition may be varied dependent upon the reactivity of the reactive ingredient, its compatibility with the metal, the tubing, the condensing medium, and whether other ingredients or treatments are needed to cause the reactive ingredient to react with or treat the surface of the particle in the manner desired. Certain reactive materials may be present as the non-reactive carrying medium, if they are slow reacting or need another component or unique conditions (e.g., e-beam, ultraviolet radiation, infrared radiation, etc.) to react or treat the surface of the nanoparticles. Other reactive materials may be introduced within the carrying tube (e.g., 22) before the dry mechanical pump, in the dry mechanical pump (as a condensing medium 26 or as a component of the condensing medium), or in the condenser or before the secondary pump 40. Similarly, any essential treatment or reaction zone may be located where expeditious within the system, along with any essential subcomponents needed for the treatment or reaction. Such subcomponents could include any of electromagnetic radiation sources, ultraviolet radiation sources (lamps, lasers, etc.), infrared radiation sources, visible radiation sources, e-beam sources, heat sources, steam sources, reactive gas sources, catalyst solutions, initiator sources, and the like. The reaction or treatment may be performed while the particles are suspended in a fluid (gas or liquid) medium as in a suspension, dispersion, fluidized bed, etc., or while the particles are settled on a support. In the latter case, it is

likely that such a process would be preferred only where the reaction is between the reactive ingredient and the particle surface, and not where the reactive medium reacts with itself to form a layer (as with monomers used to form a polymeric coating). Many variations of the process within the defined parameters of the invention are apparent to those skilled in the art, without further explanation, and those variants are intended to be included within the broad scope of the invention.

What is claimed:

1. A process of collecting reacted metal nanoparticles comprising forming a vapor of a metal that is solid at room temperature, the vapor of the metal being provided into an inert gaseous carrying medium, solidifying at least some of the metal within the gaseous carrying medium to form metal nanoparticles, combining the metal particles with a reactive gas medium, moving the metal nanoparticles in a gaseous carrying environment through a dry mechanical pumping system, and while the particles are within the dry mechanical pumping system or after the nanoparticles have moved through the dry pumping system, contacting the metal nanoparticles with an inert liquid collecting medium.

2. The process of claim 1 wherein the reactive gasesous medium material comprises a polymerizable monomer that can be polymerized to form a polymer coating on the surface of the particle.

3. The process of claim 2 wherein the inert liquid collecting medium comprises an organic liquid.

4. The process of claim 2 wherein metal particles within the dry mechanical pumping system are contacted with an inert liquid collecting medium.

5. The process of claim 2 wherein metal particles are contacted with an inert liquid collecting medium after leaving the dry mechanical pumping system.

6. The process of claim 5 wherein a vacuum system is installed to provide additional driving force to collect nanoparticles by physical filtration.

7. The process of claim 1 wherein the reactive gasesous medium comprises an ambifunctional compound with only a single chemical function that can react with the metal.

8. The process of claim 7 wherein the inert liquid collecting medium comprises an organic liquid.

9. The process of claim 7 wherein metal particles within the dry mechanical pumping system are contacted with an inert liquid collecting medium.

10. The process of claim 9 wherein the nanoparticles are also collected by physical filtration.

11. The process of claim 9 wherein the nanoparticles are collected in slurry and subsequently coated using high pressure reactor coating.

12. The process of claim 7 wherein metal particles are contacted with an inert liquid collecting medium after leaving the dry mechanical pumping system.

13. The process of claim 1 wherein the reactive gasesous medium chemically reacts directly with metal on the surface of the particle.

14. The process of claim 1 wherein the metal nanoparticles comprise a metal having a vaporization temperature between 200° C. and 3000° C.

15. The process of claim 1 wherein the metallic nanoparticles comprise at least one metal selected from the group consisting of Al, Cu, Ti, Ag, Au, Pb, Sn, Zr, and Ni.

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